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ON ACYLHALOGENAMINE DERIVATIVES AND THE BECKMANN REARRANGEMENT.

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A. W. Hofmann's[1] well-known method for preparing amines by converting acid amides into acid bromamides and treating the latter with aqueous alkali, involves a molecular rearrangement of the acid bromamides which, as Hoogewerff and van Dorp[2] later pointed out, is a perfect parallel of the Beckmann rearrangement of the oximes. In both cases an alkyl or alphyl radical (R) leaves the carbon atom holding the nitrogen halide (NHX), or the oxime (NOH) group, and attaches itself to the nitrogen atom, while the negative atom (Cl, Br), or group (OH), originally held by the nitrogen, oxidizes the carbon atom in question. The following equations give summarily the course of the reactions:

$$RCO.NHBr \rightarrow BrCO.NHR \rightarrow CO : NR + HBr;$$
$$R'RC : NOH \rightarrow R'C(OH) : NR \rightarrow R'CO.NHR.$$

The mechanism of these interesting molecular rearrangements has been the subject of some investigation and quite a

[1] Ber. d. chem. Ges., **14**, 2725 (1881); **15**, 408 (1882).
[2] Rec. trav. chim. Pays-Bas, **6**, 376 (1887).

little speculation.[1] In a study of the nature and cause of the rearrangement, attention was called by Prof. Stieglitz to the desirability of determining experimentally to what extent, if at all, the hydrogen atom in the acid bromamide group, —CONHBr, is necessary for effecting the rearrangement of the acid bromamides. According to his views "an alkali might cause an acid bromamide, RCONHBr, to lose hydrobromic acid directly, thus producing a body, $(RCO)N<$, with a univalent nitrogen atom, the reactivity of which must then be the cause of the peculiar separation of the alkyl radical, R, from the carbon atom holding the nitrogen; the very reactive univalent nitrogen atom taking the alkyl radical away from the carbon atom, isocyanates must result, and these have actually been obtained as the first tangible products of the reaction." The formation of an isocyanate as the first product of the rearrangement is also in accord with the production of the most important compounds finally obtained from acid bromamides under varying conditions, *viz.*, amines by the action of hot dilute alkalies,[2] carbamates, RNHCOOK, in the presence of cold concentrated alkali,[3] and urethanes[4] in the presence of alcohols.

At the suggestion and under the direction of Professor Stieglitz, I undertook[5] the investigation of the problem whether the Beckmann rearrangement could still proceed or would be prevented when the hydrogen atom necessary for the breaking off of hydrobromic acid had been replaced by an alkyl or an alphyl group.

The investigation had to concern itself with the two possible classes of such derivatives. In the first place we could

[1] Hofmann: *Loc. cit.*; Hoogewerff and van Dorp: Rec. trav. chim. Pays-Bas, **15**, 107 (1896). Freundler: Bull. Soc. Chim., **17**, 421 (1897); Nef: This JOURNAL, **18**, 753 (1896), Note. Ann. Chem. (Liebig). **298**, 308 (1897); **318**, 39, 227 (1901). See in particular, Stieglitz: On the "Beckmann Rearrangement," This JOURNAL, **18**, 751 (1896); **29**, 49 (1903).

[2] Hofmann: Ber. d. chem. Ges., **15**, 411, 412 (1882).

[3] Hoogewerff and van Dorp: *Ibid.*, **20**, Ref. 470 (1887).

[4] Stieglitz and Lengfeld: This JOURNAL, **15**, 215, 504 (1893).

[5] This work was begun in 1895 and has been continued, chiefly in summer vacations, ever since. A preliminary paper was published in 1896 (Ber. d. chem. Ges., **28**, 3266) to hold the field, and notices of the progress of the investigation have appeared at intervals (This JOURNAL, **18**, 753 (1896); Ber. d. chem. Ges., **34**, 1613 (1901); Proc. Chem. Soc. (London), **16**, 1 (1900), etc.)

have acylhalogenalkyl(alphyl)amines in which both the alkyl (alphyl) and the halogen are attached to the nitrogen atom, as in RCO.(NHalR'). In the second place we could have the halogen imido ethers RC(: NHal)OR', isomeric with the first series, the alkyl (alphyl) group, R', being attached to the oxygen atom. The work done on the former class of compounds will be discussed first.

When this investigation was begun only two or three compounds of this class were known. These were notably acetylethylchloramine prepared by Tscherniak and Norton,[1] and acetylchloranilide obtained by Bender.[2] Analogous bromine derivatives were not known. The methods used by the chemists mentioned failed to give good results in the preparation of other derivatives of this class, and of bromine compounds,[3] in particular, as most of these compounds are extremely sensitive to change by the action of acids, by reduction, by hydrolysis, or in the case of derivatives of the aromatic amines, by rearrangement into the acyl derivatives of halogen anilines, $H_2N(C_6H_4Hal)$. A careful study was first undertaken, therefore, to develop the special conditions and precautions for isolating these acyl halogen amides. As will be shown in the experimental part, this study was successful, both experimentally and in supplying the theoretical basis for correct work.

In the next place it was found necessary to make an experimental determination of the constitution of these acylhalogenalkyl(alphyl)amines, to decide between the two possible constitutions :

RCO.(NHalR') and RC(OHal)(: NR')
I. II.

Although important theoretical conclusions were based[4] on the generally accepted constitution (I.), it really had never been proved rigidly, and it was open, if not to decided objec-

[1] Bull. Soc. Chim., **30**, 106 (1878).

[2] Ber. d. chem. Ges., **19**, 2272 (1886).

[3] See, for example, Castoro : Gazz. chim. ital., **28**, 312 (1898) ; Oechsner de Coninck : Compt. rend., **126**, 907, 1042 (1898).

[4] See, for example, Norton and Tscherniak : *Loc. cit.*, p. 106 ; Armstrong : J. Chem. Soc. (London), **77**, 1051 (1900) ; Chattaway and Orton : *Ibid.*, **75**, 1046 (1899); etc.

tion, at least to serious doubt. Its general acceptance seems to have been based chiefly on the idea that in an acyl anilide, such as acetanilide, $CH_3CONHC_6H_5$, the nitrogen atom still holds a hydrogen atom, as in aniline, and that such a compound must, by substitution, under the influence of hypochlorous acid, give a nitrogen halide, $CH_3CO.NClC_6H_5$. It has, however, been proved that acyl amides and anilides frequently do give oxygen derivatives.[1] For instance, Comstock and Kleeberg showed that formanilide forms a silver salt from which methylphenylimidoformate, $HC(OCH_3)NC_6H_5$, is obtained by the action of methyl iodide. The metal salts undoubtedly have an analogous constitution.[2] On finding that silver formanilide gave with iodine, under the same circumstances as in the previous reaction, formyliodaniline, Comstock suggested that the iodine derivative could very well have a constitution analogous to that of the imido ethers, *viz.*, HC—(OI) : NC_6H_5, and since the iodide has the same properties as all the acylchlor- and bromanilides, it is obvious that the constitution of the latter bodies could not be based on their formation from acyl anilides. Their properties of being chlorinating or brominating agents, of being susceptible to hydrolysis, and of being readily rearranged into acyl derivatives of chlorinated or brominated anilines, $NH_2(C_6H_4X)$, would agree equally well with either of the above constitutions (I. and II.). If the bodies were not really nitrogen halides, RCON(Hal)R′, however, any deductions in regard to the "Beckmann rearrangement," as based on their behavior, would obviously have been impossible, and so a rigid experimental proof was sought at once, which would decide between constitutions I. and II.

In our first attempts to settle the question of the constitution of these bodies their behavior was such as to throw considerable doubt on their being nitrogen halides. We found first that the acyl halogen anilides do not form any cyanogen derivatives with potassium cyanide according to the equation :

[1] Comstock, Kleeberg, Wheeler, and others : This JOURNAL, **12**, 493 (1890) ; **13**, 520 (1891) ; **19**, 129 (1899) ; etc. Tafel and Enoch : Ber. d. chem. Ges., **23**, 105 (1890) Stieglitz and Dains : J. Am. Chem. Soc., **21**, 135 (1899).

[2] Hantzsch : Ber. d. chem. Ges., **34**, 3142 (1901) ; **35**, 228 (1902).

$$CH_3.CO.N(Hal).C_6H_5 + KCN \rightarrow CH_3.CO.N(CN).C_6H_5 + KHal,$$

but are always reduced to the acyl anilides. On the other hand, undoubted nitrogen chloride derivatives, like the chlordialkylamines, R_2NCl, easily give cyanamides under exactly the same conditions.[1]

$$R_2NCl + KCN \rightarrow R_2N.CN + KCl.$$

In order to make sure that the right conditions were present for Berg's reaction, the method was tried on chlorpiperidine, and cyanpiperidine was obtained without difficulty.

Secondly, it appeared from many experiments that the acylhalogenalkyl(alphyl)amines, by treatment with zinc ethyl, are simply reduced and not alkylated; for instance, the reaction

$$2R—CO—N(Hal)—C_6H_5 + Zn(C_2H_5)_2 \rightarrow 2RCO—N(C_2H_5)(C_6H_5) + ZnHal_2$$

does not take place. But an undoubted nitrogen chloride derivative, ethyldichloramine, $C_2H_5—NCl_2$, is known to give, with zinc ethyl, triethylamine.[2]

The last way taken for establishing the constitution of the acylhalogenalkylamines led to the following simple solution of the question.[3] If acetylamylamine is treated with hypochlorous acid, the corresponding acetylchloramylamine is formed:

$$CH_3CO—NH—C_5H_{11} + HOCl \rightarrow CH_3CO—NCl—C_5H_{11} + H_2O.$$

The same compound is obtained when amylchloramine[4] is acetylated by means of acetic anhydride,

$$C_5H_{11}—NHCl + (CH_3CO)_2O \rightarrow CH_3CO—NCl—C_5H_{11} + C_2H_4O_2.$$

This result proves that the acylhalogenalkylamines and anilides are really nitrogen halides, that is, derivatives of Hofmann's acid chlor- and bromamides, RCO(NHHal), and that

[1] **Berg**: Ber. d. chem. Ges., **26**, 188 (1893), Ref.
[2] **Tscherniak**: *Ibid.*, **9**, 148 (1895).
[3] **Stieglitz and Slosson**: *Ibid.*, **34**, 1615 (1901).
[4] **Berg**: Bull. soc. chim., [3], **3**, 687 (1890).

the constitution, RC(OHal)(NR'), suggested by Comstock as a possible one for them, may now be excluded without hesitation as far as the chlorine and bromine compounds are concerned.[1]

Two parts of the work on the first class of alkyl (alphyl) derivatives of the acid halogen amides, *viz.*, the determination of the special conditions for preparing them and the determination of their constitution, having been disposed of, it only remained to test whether such compounds could be made to suffer the "Beckmann rearrangement" which the mother-substances, the acid halogen amides, RCO—NH—Hal, undergo so readily. A large number of experiments with all varieties of acylhalogenalkylamines and acylhalogenalphylamines led to the important conclusion that in no case could a Beckmann rearrangement be effected. In some cases, for example, with benzchloranilide, $C_6H_5.NCl.C_6H_5.CO$, it was possible to show that the rearrangement did not occur even to a minimal extent, since not even traces of diphenylamine, which is easily detected, could be found.

It was shown above, (page 291) that the acid halogen amides must give by replacement of the hydrogen atom of the group —CONHHal, besides the alkylated (alphylated) nitrogen derivatives —CO(NRHal) just discussed, a second class of isomeric ethers, —C(OR)(: NHal), whose relation to the Beckmann rearrangement was included in this investigation. In contrast to the bodies just dealt with, these imido ethers presented a comparatively simple problem. The methods for their preparation and their constitution had been definitely established by Stieglitz,[2] who prepared methyl chlor- and bromimidobenzoate, and they had been proved by him to be most remarkable for their stability as nitrogen halides. My work on these bodies was chiefly directed towards the preparation of stereoisomers and the effecting of the Beckmann rearrangement. On the basis of Hantzsch and Werner's[3] theory

[1] So little is known about the corresponding iodine derivatives, and the character of hypoiodous acid approaches so near that of a base that no conclusion as to the constitution of Comstock's formiodanilide should be based on the above work with hypochlorous acid. Formiodanilide may very well stand closer to silver formanilide than to formchloranilide. J. STIEGLITZ.

[2] This JOURNAL, **18**, 751 (1896).

[3] Ber. d. chem. Ges., **25**, 33 (1892); **29**, 1146 (1896).

of stereoisomerism (syn and anti) produced by a doubly-linked nitrogen atom, as in the oximes, the halogen imido ethers might exist in the two stereoisomeric forms,

$$\begin{array}{c} R—C—OR' \\ \| \\ Hal—N \end{array} \quad \text{and} \quad \begin{array}{c} R—C—OR' \\ \| \\ N—Hal \end{array}.$$

Only the former class would be expected to be directly capable of undergoing a Beckmann rearrangement of the molecule.[1] Although solid chlorimido ethers of admirable stability were obtained, all efforts at recognizing stereoisomers, or at converting the compounds obtained into other modifications, resulted in failure.[2] None of the halogenimido ethers investigated gave the least sign of undergoing the Beckmann rearrangement.

It would appear, therefore, that the presence of the hydrogen atom (H') of the acylamine halides, RCO—NH'Hal, is essential for the successful "Beckmann rearrangement" of the molecules, since neither class of their alkyl derivatives is capable of undergoing the rearrangement in question.

EXPERIMENTAL PART.

The Preparation of Alphylacylhalogenamines.

The successful preparation of the chlorine and bromine compounds of this class was found to be dependent on observing a number of interesting conditions, which follow from the peculiar tendency of these bodies to suffer chemical change. Bender had obtained phenylacetylchloramine by treating acetanilide with an aqueous extract of bleaching-powder and acidulating the mixture with acetic acid. His directions are so indefinite that some chemists have failed entirely to prepare phenylacetylchloramine by his process. For example, Castoro[3] says Bender's reaction is impossible

[1] Werner: *Loc. cit.*

[2] Like failure, it will be remembered, has so far attended all efforts of Hantzsch and others to prepare stereoisomeric derivatives, : C : NX, in which X was, for instance, C_6H_5—, —COOR, or any group in fact other than —OH (the oximes) or —NHAlphyl (the hydrazines). Ber. d. chem. Ges., **27**, 1248 (1899), etc.

[3] Gazz. chim. ital., **28**, 312 (1898); compare Armstrong: J. Chem. Soc. (London), **77**, 1047 (1900).

and that he gets by all possible variations of the proportions of acetanilide, acetic acid, and hypochlorite no active nitrogen halide derivatives but only two inactive bodies, parachloracetanilide and a dichloracetanilide.[1] While, as a matter of fact, the active acetylchloranilide can readily be obtained by following Bender's directions carefully, neither the yield nor the purity of the compound is satisfactory. The method failed utterly in attempts to use it for preparing analogous active nitrogen bromide compounds of the acylanilides,[2] only inactive derivatives of the bromanilines resulting with the bromine attached to the benzene nucleus of the anilines.

The first fact of which cognizance must be taken in the preparation of these nitrogen halides is that the reaction by which they are formed is reversible :[3]

$$RCO—NHR' + HOHal \rightleftarrows RCO—NHalR' + H_2O.$$

The mass law requires, therefore, an excess of hypochlorous or hypobromous acid to effect a tolerably complete transformation except in those cases where the product is very insoluble. In going from the derivatives of hypochlorous to hypobromous and hypoiodous acid, the hydrolysis of the above nitrogen halides by water seems to become progressively more marked, and, therefore, to play a more important rôle in their preparation, as the atomic weight of the halogen increases. This was verified experimentally. The phenylacylbromamines were found by me to stand between the analogous chlorine and iodine derivatives. Phenylacetylchloramine is rather stable even towards boiling water, phenylacetylbromamine can be prepared in the presence of water, but it is slowly decomposed, even at ordinary temperatures, by water (see below), and phenylformyliodamine could be prepared[4] only when water was carefully excluded.

In the next place, where R' in the above reaction is an aromatic radical, the nitrogen halide with its reactive halogen

[1] Oechsner de Coninck (Compt. rend., **126**, 907, 1042 (1898)) obtained no nitrogen halides by the action of hypochlorites on amides and amines.

[2] Slosson : Ber. d. chem. Ges., **28**, 3266 (1896) ; see also Seliwanow : *Ibid.*, **25**, 3620 (1892) ; Jacoby : J. prakt. Chem., [2], **37**, 50 (1888).

[3] Seliwanow : *Loc. cit.*

[4] Comstock and Kleeberg : This JOURNAL, **12**, 500 (1890).

atom is very readily transformed into the stable isomeric acyl derivative of the halogenated anilines, according to

$$RCO.NHalC_6H_5 \rightarrowtail RCO.NH(C_6H_4Hal).$$

As the latter reaction is non-reversible, the preparation of the nitrogen halides may prove an utter failure if this transformation is not prevented. This is the chief source of failure in making these compounds. The transformation was found to proceed gradually under the influence of moisture, and very much more rapidly by the action of acids. It is also caused by the action of heat.[1]

As the phenylacylbromamines are much more sensitive to water and acids (see below) than the chloramines, only their transformation-products are obtained if acids even of ordinary weakness (*e. g.*, acetic acid) are used in preparing them. The hypobromous acid necessary for their formation must be liberated by such weak acids as boric acid[2] or carbonic acid,[3] the concentration of whose hydrogen ions can be still further

[1] The first two influences are undoubtedly identical fundamentally, water being an exceedingly weak acid. The slow transformation under the influence of water, the vastly increased rate of change in the presence of acids, and the fact that a number of these compounds when dry (see pages 304–5 below) are comparatively stable towards heat and are only very slowly transformed by it, indicate that in aqueous solution this transformation is due rather to a sequence of two reactions, *viz.*:

$$RCO.NHalC_6H_5 + H_2O \rightleftharpoons RCO.NHC_6H_5 + HOHal \quad (1),$$

and

$$RCO.NHC_6H_5 + HOHal \rightarrowtail RCO.NHC_6H_4Hal + H_2O \quad (2),$$

than to a direct molecular rearrangement or migration of atoms:

$$RCO.NHalC_6H_5 \rightarrowtail RCO.NHC_6H_4Hal \quad (3).$$

As the acylalphylbromamides are much more sensitive to water and acids than the chlorides, we find in this behavior the reason why they were never successfully isolated and the transformation-products alone were obtained, until in 1896 Slosson and I avoided the use of any but the weakest acids in preparing them. (See Stieglitz and Slosson: Ber. d. chem. Ges., **28**, 3267 (1896); Proc. Chem. Soc. (London) **16**, 1 (1900); Armstrong: J. Chem. Soc. (London), **77**, 1047 (1900); Chattaway and Orton: *Ibid.*, **77**, 134 (1900)). Whether the transformation under the influence of heat is due to a molecular rearrangement or, rather, to a mutual chlorination (bromination) of two molecules,

$$2RCO.NHalC_6H_5 \rightarrowtail 2RCO.NHC_6H_4Hal,$$

remains an open question, which could be decided by determining the velocity of the reaction. Since this was written Blanks has shown by velocity determinations that the reaction consists of a monomolecular rearrangement. Rec. trav. chim. Pays-Bas., **21**, 366 (1902). See also Armstrong: *Loc. cit.* J. Stieglitz.

[2] Slosson: *Loc. cit.*

[3] Slosson: *Loc. cit.*; Chattaway and Orton: J. Chem. Soc. (London), **75**, 1046 (1899), etc.; Küster: Ztschr. Elektrochem., **4**, 110.

diminished by using a bicarbonate, or carbonic acid in the presence of a bicarbonate.

In the last place it follows from the above discussion that in the purification of these nitrogen halides by recrystallization, aqueous solvents and moisture must be rigidly excluded, besides, obviously, such solvents as are very easily chlorinated or brominated.

The conditions, then, for successfully preparing even rather unstable representatives of the alphylacylhalogenamines are the use of a considerable excess of the hypo acid, the exclusion of more than minimal quantities of hydrogen ions, best obtained from very weak acids, and the exclusion of moisture in the process of purification. The avoidance of an unnecessary rise of temperature may be added as a further precaution.

For chlorinating compounds insoluble in water the following method was found useful: Thirty grams of sodium hydroxide are dissolved in 100 cc. of water and a weighed amount of chlorine, nearly enough to saturate it, is absorbed in the cold solution. With ordinary caustic soda, which has been exposed to the air and therefore has taken up some water and carbonic acid, between 20 and 24 grams of chlorine may safely be absorbed, but the operation must be stopped before decomposition sets in through an excess of chlorine. A solution so prepared contains very nearly the theoretical amount of active chlorine, one-half the total. It can be kept in a cool place for several days without material loss of strength. If to a sufficient quantity of this solution be added the calculated amount of the amide dissolved in alcohol, which is saturated with boric acid, the chlorine compound is precipitated on diluting with water, and can be filtered by suction and dried on a porous clay plate; or, if it is very unstable, the reagents may be mixed in a separatory funnel, together with powdered ice, and the nitrogen halide extracted at once with ether. Bromine compounds can be made in the same way, by using a solution prepared by dissolving bromine in a slight excess of potassium hydroxide solution, or by shaking it with mercuric oxide and water.

All the nitrogen halides set free iodine, either from potas-

sium iodide or from hydriodic acid, and they can be analyzed by dropping them into a slightly acidified solution of potassium iodide and titrating the released iodine with a N/10 solution of thiosulphate. Where the compound is very insoluble in water, it is necessary to dissolve it in alcohol or in a mixture of ether and alcohol. The determination of the halogen as silver halide does not necessarily indicate the purity of the compound in the case of anilides and naphthalides, because the isomers with halogen in the ring, which are the chief impurities, give by Carius' method the same analytical figures as the nitrogen halides. It is best to titrate the iodine as quickly as possible, for there are sometimes secondary reactions with the free iodine which cause too low results.[1]

Phenylacetylchloramine (*Acetylchloraminobenzene*), $CH_3CO—NClC_6H_5$.

This compound may be formed in acid, alkaline, or neutral solutions of hypochlorites, but a slightly alkaline solution is best, and, after trying a great many methods, the following was found to give the most satisfactory results:[2] Twenty grams of acetanilide are dissolved in 4 liters of water and the solution cooled to at least 10°. Chlorine is passed into a cold solution of sodium carbonate (10 per cent) until a test with a few cubic centimeters shows that the solution will precipitate ten times its volume of the acetanilide solution; then the required quantity of this hypochlorite solution is poured into the acetanilide solution and shaken. The chlorine compound comes down at once as a flocculent precipitate. It is filtered, washed, and dried. The yield is 20 to 24 grams (theoretical 25 grams). If the hypochlorite solution is deficient in strength or quantity, the precipitate forms slowly in fine needles, isolated or in bundles. If too strongly alkaline, the solution turns brown, has the odor of isocyanide, and the chlorine compound reverts to acetanilide. If the solution is too strongly acid, or if there is much free chlorine, parachloracetanilide is the sole product. Phenylacetylchloramine

[1] Compare Behrend and Schreiber: Ann. Chem. (Liebig), **318**, 381 (1901).

[2] For other methods, see Bender: Ber. d. chem. Ges., **19**, 2272 (1886); Chattaway and Orton: J. Chem. Soc (London), **79**, 277 (1901); Armstrong: *Ibid.*, **77**, 1047 (1900).

is quite stable when pure and dry, and it can be preserved for days without material decomposition. It melts at 91°.

0.2463 gram substance required 28.98 cc. N/10 thiosulphate.

	Calculated for C_9H_8NOCl.	Found.
Cl	20.91	20.86

A great many experiments were made on the decomposition of phenylacetylchloramine with potassium hydroxide and sodium methylate, but in no case was it possible to detect methylaniline or any derivative of it, which would be the product if a Beckmann rearrangement had taken place. From 18 to 30 grams of the substance were used in each test, but acetanilide was the sole product identifiable whether the reaction-product was worked out by precipitation, extraction, or distillation. Both hot and cold solutions of potassium hydroxide were used, and both 10 and 20 per cent strengths. When hot strong alkali was used, the solution turned brown and had a disagreeable odor, apparently of isocyanide, and there was a little tarry matter formed. The acetanilide was, however, recovered almost quantitatively in every case in a nearly pure state, and from the slight residues the only basic compound obtained after saponification was aniline in which no methylaniline could be detected.

A series of experiments with solutions of sodium methylate, cold and hot, strong and weak, gave similar results, and none of the products of a Beckmann rearrangement could be found. Even when 30 grams of the chlorine compound were used, acetanilide was the sole product in quantity sufficient to identify, although there was evidence of further decomposition in the red color of the extract in ligroin, which in acid alcohol gave a purple solution of great tinctorial power.

Methyl Phenylmethylcarbamate, $(C_6H_5NCH_3)COOCH_3$.—As this compound is one which might result from a Beckmann rearrangement of phenylacetylchloramine with sodium methylate, its properties were determined by preparing it. Redistilled methylaniline (16 grams) was shaken with the same volume of water to an emulsion, and to the solution cooled to 0° was added 7 grams of methyl chlorcarbonate from small

bulbs with capillary tubes. The mixture was warmed for half an hour, then cooled, and hydrochloric acid added to acid reaction. The ether extract was dried over calcium chloride and distilled twice. The product, the methyl ester of phenylmethylcarbamic acid, is a light-yellow oil, easily soluble in ether and ligroin. It is dissolved by heating it in concentrated hydrochloric acid but is not attacked by a solution of sodium hydroxide. It has a fishy odor and boils at 235°.

0.4070 gram substance gave 44 cc. N at 25° C. and 743.8 mm.

	Calculated for $C_9H_{11}O_2N$.	Found.
N	8.42	8.43

Several attempts were made to replace the chlorine atom in phenylacetylchloramine with an ethyl radical by the use of zinc ethyl,[1] but in no case was there evidence of such a reaction.

Dry phenylacetylchloramine (14 grams) was dropped gradually into a solution of zinc ethyl (5 grams) in absolute ether in a flask fitted with a reflux condenser. At each addition of the chloranilide there was an evolution of a gaseous hydrocarbon, which was collected but not analyzed. A stream of carbon dioxide was carried through the apparatus during the operation. At the end the ether was evaporated and water added. Repeated extraction of the acid and alkaline solution with ether gave acetanilide as the only product, and this, when purified, amounted to 11.3 grams. Repeating the experiment with the same quantities of the reagents, parachloracetanilide was the chief product obtained. Evidently the molecular transformation was caused by the energy liberated in the reaction. In the residues the products of saponification, acetic acid and aniline were found in small quantity, but no derivatives of ethylaniline which would result from the substitution of chlorine by that radical or methylaniline from a Beckmann rearrangement could be detected.

Phenylacetylchloramine (13 grams) dissolved in 50 per cent alcohol and treated with potassium cyanide (5 grams) gave acetanilide and parachloracetanilide as the sole products.

[1] Tscherniak: Bull. soc. chim., [2], **25**, 166 (1896); Ber. d. chem. Ges., **9**, 148(1896).

There was no evidence of the substitution of chlorine by cyanogen according to Berg's reaction.[1]

Piperidyl Cyanide by Berg's Reaction.—In order to test the generality of Berg's reaction and to assure myself that I understood the conditions under which it took place, piperidyl cyanide was prepared by the following method.[2] Six grams of chlorpiperidine, prepared by dropping 10 grams of piperidine into a boiling solution of bleaching-powder,[3] was dissolved in alcohol and treated with 3 grams of potassium cyanide in fine powder. The reaction takes place immediately and the alcohol is heated to boiling. After distilling off the alcohol, taking up the residue with ether, and drying it over potassium hydroxide, the piperidyl cyanide was distilled in a vacuum (30 mm.) between 122° and 124° C. It is a colorless, fragrant oil, insoluble in water.

The identity of the piperidyl cyanide was proved by converting it into piperidyl urea by heating it with 50 per cent sulphuric acid for half an hour on a water-bath. After neutralizing the solution with sodium hydroxide and extracting the mixture with ether, the urea was obtained by evaporation of the ether. It was recrystallized from water and compared with piperidyl urea made by Cahours' method.[4] A mixture of the two preparations melted at the same point (103° C.).

Parachloraniline.—On account of the ease with which the chlorine in acetylchloranilide can be made to enter the para position and the resulting compound can be saponified, use can be made of this reaction in the preparation of *p*-chloraniline. For making this in quantity, the following process was found more convenient than the methods published: Dissolve 10 to 15 grams of acetanilide in a liter of water, cool somewhat, and pass in chlorine as long as the white precipitate of *p*-chloracetanilide is formed. Filter and heat the chloracetanilide for an hour at 150°, with enough concentrated sulphuric acid to

[1] Ann. chim. phys., [7], **3**, 353 (1894).

[2] The same cyanide has since been prepared in another way by Wallach and Samann: Ber. d. chem. Ges., **32**, 1873 (1899).

[3] Lellmann and Geller; *Ibid.*, **21**, 1922 (1888).

[4] Ann. chim. phys., [3], **38**, 84 (1853).

dissolve it. Pour the mixture into water, make the solution alkaline with some hydroxide to precipitate most of the parachloraniline, and extract the filtrate with ether to get the rest. Purify the compound by dissolving it in water, boiling the solution with animal charcoal, and filtering. By concentrating the water solution, parachloraniline crystallizes out in cubes or needles. The yield is almost quantitative.

Phenylacetylbromamine (*Acetylbromaminobenzene*), $CH_3CO(C_6H_5NBr)$.—This compound was first made by adding a solution of potassium hypobromite to a saturated aqueous solution of acetanilide and then passing a stream of carbon dioxide into the solution. If the acetanilide solution contains borax or boric acid, the bromine compound is precipitated without using carbon dioxide. A saturated solution of acetanilide, prepared by dissolving about 5 grams in a liter of water and saturating it with borax and boric acid, is cooled to 0° and filtered. To this is added an excess, even twice the theoretical amount, of hypobromite solution made by dissolving bromine in 10 per cent potassium hydroxide. If both solutions are kept cold, best with powdered ice, the phenylacetylbromamine is slowly precipitated, and after filtering can be freed from a small quantity of parabromacetanilide by fractional crystallization from ether or ligroin. It is precipitated in yellow flakes or four-pointed stars, and melts at 94° to 95°, changing to parabromacetanilide.

0.1748 gram substance required 16.32 cc. N/10 thiosulphate.

	Calculated for C_8H_8ONBr.	Found.
Br	37.35	37.34

This bromacetanilide is very much more unstable than the corresponding chlorine compound, and changes into parabromacetanilide in a few minutes when in warm and moist air. With ammonium hydroxide it gives off nitrogen as do all the compounds of this class. In numerous experiments with this compound only the two forms of decomposition were observed: with acids, it is transformed to parabromacetanilide, and with alkalies acetanilide is regenerated. None of the products of a Beckmann rearrangement were ever found.

Phenylformylchloramine (*Formylchloraminobenzene*), HCO. $NClC_6H_5$.—This compound is precipitated in crystalline form by adding a solution of hypochlorous acid, made by running chlorine into a 10 per cent solution of sodium carbonate, to an ice-cold, saturated, aqueous solution of formanilide and shaking violently. The strength of the hypochlorous solution is ascertained by titration and an excess is used. The substance melts at 44°. It can be heated even to 120° without much decomposition. Above this temperature it gives off acid vapors accompanied with a slight odor, apparently of isocyanate. It can be recrystallized from ether, ligroin, or acetic acid, but it decomposes violently with ammonia, or when heated with absolute alcohol. Hydrochloric acid and many other reagents convert it into the isomeric formyl-*p*-chloranilide.

0.1273 gram substance required 16 cc. N/10 thiosulphate.

	Calculated for C_7H_6ONCl.	Found.
Cl	22.79	22.34

For comparison, formyl-*p*-chloranilide was also made by boiling 1 gram parachloraniline with 3 grams formic acid for half an hour. The excess of formic acid is distilled off and the residue poured into cold water. It melts at 101° C. It is soluble in ether, chloroform, or hot water, but insoluble in ligroin. Recrystallized from ether it forms colorless parallelograms with diamond markings, similar in form to methylbenzamide.

Phenylformylbromamine (*Formylbromaminobenzene*), $HCO—NBrC_6H_5$.—To prepare this a one per cent solution of formanilide in water, saturated with boric acid, is cooled to 0° and a little more than the calculated quantity of potassium hypobromite solution is added. Instead of using boric acid, a stream of carbon dioxide may be run in after the addition of the hypobromite. In either case a light-brown precipitate of formylbromaminobenzene is slowly formed, which can be recrystallized from ether or ligroin in needles which are only slightly yellow and melt at 79° to 80°. The compound decomposes spontaneously even in dry air, and attacks ammonia

water violently, giving off nitrogen. By acids, alkalies, and heat it is readily converted into parabromformanilide (m. p. 119°).

0.1678 gram substance required 16.6 cc. N/10 thiosulphate.

	Calculated for C_7H_6ONBr.	Found.
Br	39.95	39.55

Phenylbenzoylchloramine (*Benzoylchloraminobenzene*), $(C_6H_5CO)NClC_6H_5$.—The insolubility of benzanilide in water makes it rather difficult to prepare the chlorine derivative by the customary methods,[1] but the following procedure gives a good yield of excellent purity. Two grams of benzanilide are dissolved in 200 cc. of alcohol with 10 grams of boric acid. To this is added 10 cc. of a solution of sodium hypochlorite containing 0.07 gram or more of active chlorine per cubic centimeter, both solutions being kept cold. After shaking and filtering the mixture with the pump, water is added and the benzoylchloraminobenzene appears as a white, flocculent precipitate. It is filtered and dissolved in ether. On adding light ligroin and evaporating the mixture in a vacuum-desiccator it forms large, transparent crystals.

0.1091 gram substance required 9.39 cc. N/10 thiosulphate.

	Calculated for $C_{13}H_{10}NOCl$.	Found.
Cl	15.30	15.22

The substance is easily soluble in ether and alcohol but less soluble in ligroin. It melts, without decomposition, at 81°.5 to 82°,[1] and it is still active with potassium iodide after it has been heated to 160° and turned slightly yellow. Above this temperature it becomes rapidly darker and gives off a little vapor, which is, judging from its odor, benzoyl chloride. The chief substance formed, however, is parachlorbenzanilide. This compound is also the result of boiling with water. Ammonium hydroxide attacks the nitrogen halide slowly in alcoholic solution.

Phenylbenzoylchloramine dissolved in alcohol and treated with a little sodium hydroxide and warmed, is reduced at

[1] Slosson: Ber. d. chem. Ges., **28**, 3269 (1896): Chattaway and Orton: J. Chem. Soc. (London), **75**, 1053 (1899). They give the melting-point as 77°.

once to benzanilide, as was proved by taking the melting-point of the reaction-product mixed with known benzanilide. The crude product of the reaction tested for diphenylamine by hydrochloric and nitric acids gave no coloration. A portion of the same mixture, to which a minute particle of diphenylamine had been added, gave an intense indigo-blue. So it is positive that the Beckmann rearrangement does not take place to the slightest extent.

For comparison with the product obtained from benzoylchloraminobenzene by the migration of the chlorine atom from the nitrogen to the aromatic nucleus, parachlorbenzanilide was prepared from benzoyl chloride and parachloraniline. When recrystallized from hot water, it appeared in fine cubical crystals. It had the melting-point 187° to 187°.5, instead of 183° to 184° as reported by Hantzsch.[1]

Paratolylformylchloramine (*Formylchloramino-p-toluene*), $CHO.NClC_6H_4CH_3$.—Adding 20 cc. of a 10 per cent solution of formyl toluide in alcohol with a little acetic acid to 100 cc. of a solution of bleaching-powder (1 cc. = 0.008 gram chlorine) precipitates formylchlortoluide. When dissolved in hot ligroin, it separates, on cooling, in beautiful clusters of crystals, melting at 49° to 50° and decomposing at 140°.

0.1122 gram substance required 13.09 gram N/10 thiosulphate.

	Calculated for C_8H_8NOCl.	Found.
Cl	20.94	20.77

Paratolylformylbromamine (*Formylbromamino-p-toluene*), $CHO—NBrC_6H_4CH_3(p)$.—To prepare this a saturated solution of formyl paratoluide in water is added to an ice-cold solution of potassium hypobromite until a flocculent precipitate is formed. The bromine compound slowly forms in flakes by shaking. It is filtered rapidly, dissolved in a very little ether, several times its volume of light ligroin is added, and the solution is quickly evaporated by a blast or by a vacuum-pump. It is pure white and melts at 80°, decomposing at slightly higher temperatures. It is extremely unstable

[1] Ber. d. chem. Ges., **24**, 56 (1891).

and rapidly turns red on exposure to moist air, giving off free bromine.

0.1314 gram substance required 11.60 cc. N/10 thiosulphate.

	Calculated for C_8H_8ONBr.	Found.
Br	37.35	35.30

α-Naphthylformylchloramine (*Formylchloramino-α-naphthalene*), HCO—($C_{10}H_7NCl$).—Adding an alcoholic solution of formyl-α-naphthalide with a little acetic acid to a large amount of calcium hypochlorite solution gives, after a few minutes' shaking in the cold, a precipitate of the chloramine. It is very soluble in chloroform but crystallizes best from ligroin. The melting-point is 63°. It is extremely unstable, as it is decomposed quickly by water at ordinary temperatures. An ethereal solution, brought over caustic potash to dry it, is at once attacked, the ether boiling and turning red.

0.1146 gram substance required 9.8 cc. N/10 thiosulphate.

	Calculated for $C_{11}H_8ONCl$.	Found.
Cl	17.25	15.13

β-Naphthylformylchloramine (*Formylchloramino-β-naphthalene*), HCO—($NClC_{10}H_7$).—Adding an alcoholic solution of formyl-β-naphthalide, acidified with acetic acid, to a solution of calcium hypochlorite, gives a yellow precipitate, naphthylformylchloramine. It is easily soluble in chloroform, from which it is precipitated by ligroin. It is best recrystallized from hot ligroin (70° to 80°). The melting-point is 75°. It decomposes violently with an alcoholic solution of caustic potash.

0.1096 gram substance required 10.30 cc. N/10 thiosulphate.

	Calculated for $C_{11}H_8ONCl$.	Found.
Cl	17.25	17.26

β-Naphthylformylamine and Hypobromous Acid.—An alcoholic solution of formyl-β-naphthalide added to potassium hypobromite solution gave a yellow precipitate which, when crystallized from alcohol, melted at 164°. This compound was inactive toward potassium iodide, and on saponification, by heating an hour with 10 per cent potassium hydroxide,

gave a flaky, white compound containing bromine, and melting at 61° when recrystallized from water and from alcohol. This is probably 1-brom-2-aminonaphthalene (m. p. 63°), and if so, it shows that the bromine atom migrates easily to the ortho position in the aromatic ring. This is the usual reaction with all halogen aryl amides when the para position is occupied.

Varying the conditions of precipitation gave unpromising gums composed of some active nitrogen bromide and other bromine derivatives of formylnaphthalide, and no further attempts were made to isolate the compounds.

Formyl-α-naphthalide also gave unsatisfactory results when attempts were made to brominate it. An alcoholic solution of the naphthalide added to hypobromite solution gave an active yellow precipitate, which, however, was so unstable that, on filtering, it instantly became hot and charred.

α-Naphthylacetylchloramine (*Acetylchloramino-α-naphthalene*), $C_{10}H_7NCl—CH_3CO$.—An alcoholic solution of acetyl-α-naphthalide with a little acetic acid added to an excess of calcium hypochlorite solution gives, after a few minutes, a precipitate of the chlorine compound. It can be recrystallized from hot ligroin in fine, pure-white crystals, melting at 75°.

0.1150 gram substance required 10.24 cc. N/10 thiosulphate.

	Calculated for $C_{12}H_{10}NOCl$.	Found.
Cl	16.12	15.78

Halogen Derivatives of the Acyl Alkyl Amides.

Compounds of the type RCO—NHalR', whether R is an alphyl or alkyl radical, are much more stable where R' is an alkyl group than where it is an alphyl radical, because there is no tendency of the halogen atom to replace the hydrogen of an alkyl group as it does the hydrogen in an aromatic ring. It is possible, therefore, in such cases, and on trial it was found desirable, to attach chlorine to nitrogen by using the almost neutral solution made by dissolving chlorine in water instead of the usual alkaline calcium or sodium hypochlorite solution, or the acid solution obtained by acidifying these with weak acids such as acetic, carbonic, or boric. In this

case, as in the others, hypochlorous acid is still doubtless the reagent effecting the change, for Jawkowkin[1] has shown that chlorine water contains hypochlorous acid as well as hydrochloric.

To determine whether chlorine acts directly on the amides or only when in aqueous solution and, therefore, presumably hydrolyzed, 1 gram of ethylbenzamide was dissolved in chloroform with a few drops of potassium hydroxide solution and a stream of chlorine passed in for some time. On evaporating the solvent, the unchanged ethylbenzamide was recovered with no trace of an active nitrogen chloride.

Ethylbenzoylchloramine (*Benzoylchloraminoethane*), $C_6H_5CO—(NClC_2H_5)$.—Ethylbenzoylchloramine may be made in the usual way by using hypochlorite solutions, but the best results were obtained by dropping as aturated solution of ethylbenzamide in alcohol into about ten times its volume of chlorine water, which must not be too cold but at about 10°. The oily drops may be made to crystallize by adding a crystal of ethylbenzoylchloramine, or, if there is none at hand, by heating a little of the mixture until it crystallizes on cooling and shaking, and then adding this to the mixture. More chlorine water may be used to give another crop. The compound is soluble in ether, alcohol, and hot water, and may be crystallized from the last in the form of very fine, white needles. The melting-point is 53°.5.

0.1540 gram substance required 16.8 cc. N/10 thiosulphate.

	Calculated for $C_{18}H_{10}ONCl$.	Found.
Cl	19.31	19.37

The stability of the compound is quite remarkable. It is not decomposed by boiling water, and it melts without change. Warming with ammonia water reduces it rapidly.

The corresponding chlorine derivative of metanitrobenzamide is not so easily prepared. Ethylnitrobenzamide was made by the action of metanitrobenzoyl chloride on ethylamine hydrochloride in the presence of an alkali. It can be recrystallized from hot water and melts at 120°. Attempts to

[1] Ztschr. phys. Chem., **29**, 613 (1899).

chlorinate this compound either by using hypochlorite solutions or chlorine water gave only traces of an active nitrogen halide.

Ethylbenzchloramide (1.8 grams) dissolved in alcohol was treated with potassium cyanide (0.7 gram). After warming for some time, the alcohol was distilled off, water added, and the solution extracted with ether. The ethereal solution gave only crystals of ethylbenzamide. On grinding together in a mortar ethylbenzoylchloramine (1.5 grams) with potassium cyanide (0.5 gram), the mixture became liquid and gave off a strong odor of hydrocyanic acid. In ten minutes the mass again became solid. It was extracted with ether which, on evaporation, gave crystals of ethylbenzamide, melting at 68° to 69°, so there were no other products in appreciable quantity. Therefore Berg's reaction does not take place under these conditions.

Ethylbenzoylchloramine (2 grams) was dissolved in dry ether, placed in the bottom of a tall cylinder filled with carbon dioxide, and a small glass bulb containing about 1 gram of zinc ethyl was dropped in. Although the solution was cooled to 0° the reaction was violent. On filtering and evaporating the solution, ethylbenzamide alone remained, having a melting-point of 66° without recrystallizing. There was, therefore, no evidence of any substitution of chlorine by ethyl.

Methylbenzoylchloramine (*Benzoylchloraminomethane*), $(C_6H_5CO)NClCH_3$.—Methylbenzoylchloramine may be made by dissolving methylbenzamide in alcohol, dilute acetic acid, or water, and adding the solution to a solution of calcium hypochlorite or sodium hypochlorite, or simply to chlorine water. A saturated aqueous solution of the amide with chlorine water, both ice-cold, was found to give the best results. As the compound is somewhat soluble, it is usually necessary to extract with ether. Methylbenzoylchloramine is a colorless oil, heavier than water. It does not solidify at a temperature of —16°, even when inoculated with a crystal of ethylbenzoylchloramine. This substance was tried because it, too, was difficult to solidify, and because it was thought that the two compounds might be isomorphous.

0.2035 gram substance required 23.15 cc. N/10 thiosulphate.

	Calculated for C_7H_8ONCl.	Found.
Cl	20.9	20.2

Methylbenzoylchloramine is decomposed by boiling with water or with dilute potassium hydroxide solution, by a strong solution of potassium hydroxide in the cold, by heating alone, and on long standing in a desiccator. Methylbenzamide is formed in all these cases and Beckmann's rearrangement does not take place. A sample containing 15.7 per cent chlorine was heated on a water-bath for half an hour, and was then found to contain 14.2 per cent active chlorine. Yet in some cases, on the evaporation of its ethereal solution by an air-blast, it decomposed spontaneously with the production of much heat. It cannot be distilled without decomposition, even in a vacuum. Concentrated hydrochloric acid attacks it, giving off chlorine. Ammonia water decomposes it slowly, even in the cold, regenerating the amide.

The difference in stability between this compound and the homologous ethylbenzoylchloramine is very marked and the reagents which decompose the former completely have but very little effect on the latter. Evidently the ethyl group exercises a protecting influence over the halogen which is attached to the same nitrogen, which may be due to stereochemical causes.

Amylacetamide.—Amylacetamide was prepared by slowly mixing an ethereal solution of isoamylamine (2 molecules) with an ethereal solution of the calculated quantity of acetyl chloride (1 molecule). After adding water to dissolve the amylamine hydrochloride, the ether was evaporated and then the amylacetamide distilled at a temperature of 230° to 232°. It is an oil and forms a pale-yellow platinum salt when chlorplatinic acid is mixed with its alcoholic solution and ether is added.

Amylacetylchloramine (*Acetylchlor-4-amino-2-methylbutane*), $CH_3CO—(NClC_5H_{11})$.—Adding isoamylacetamide to a solution of calcium hypochlorite gives the chlorine derivative as an oil, which, since it could not be distilled even in a vacuum

nor solidified in a freezing-mixture, could not be perfectly purified.

I. 0.3896 gram substance required 45.25 cc. N/10 thiosulphate.

II. 0.2552 gram substance required 30 cc. N/10 thiosulphate.

	Calculated for $C_7H_{14}ONCl$.	Found. I.	II.
Cl	21.66	20.48	20.85

This compound is remarkably stable. It was not completely decomposed on standing two days in acid or in ammonia solution, nor on being warmed with these. Boiling water, however, decomposes it explosively. It is miscible with glacial acetic acid and is not decomposed by it in the cold. It can be dissolved in acetic acid and reprecipitated by the addition of an alkali.

Amylacetylchloramine having been prepared by the action of hypochlorous acid on amylacetamide, the method of introducing the chlorine and the acetyl group in the reversed order was tried by acetylating amylchloramine, in order to prove that in compounds of this class the halogen is really held by the nitrogen atom (see page 291). Isoamylchloramine was prepared in a way similar to that used by Berg.[1] Ten grams of the amylamine hydrochloride were dissolved in water and added to 50 cc. of sodium hypochlorite solution containing 8 per cent active chlorine. The oil separates at once and can be dissolved in ligroin (35° to 40°), washed with water, and the ligroin evaporated off in a vacuum-desiccator. A manometer is used to indicate when the ligroin is expelled. The chloramine is extremely unstable, and unless quickly purified, it goes over spontaneously, and sometimes instantaneously, into amylamine hydrochloride and the dichloramine.

0.1428 gram substance required 23.51 cc. N/10 thiosulphate.

	Calculated for $C_5H_{12}NCl$.	Found.
Cl	29.17	29.20

[1] Bull. soc. chim., [3], **3**, 687 (1890).

This amylchloramine was added to a little more than its volume of acetic anhydride. The two do not mix when cold, but on allowing them to reach room temperature reaction takes place, producing a slight rise in temperature. Glacial acetic acid was then added, and afterwards water. The amylacetylchloramine separated from the solution and could be washed with water, or could be dissolved with ligroin or ether and washed and obtained by evaporating off the solvent. The colorless oil appears identical in all respects with that obtained by chlorinating the amylacetamide, and although it was not obtained absolutely pure, as it could not be distilled in a vacuum nor solidified, the results are sufficiently close to identify it.

I. 0.3961 gram substance required 46.02 cc. N/10 thiosulphate.

II. 0.1079 gram substance required 12.93 cc. N/10 thiosulphate.

III. 0.1012 gram substance required 11.85 cc. N/10 thiosulphate.

	Calculated for $C_7H_{14}ONCl$.	Found. I.	II.	III.
Cl	21.66	20.60	21.25	20.80

Considering the ease with which the acetylation takes place and the low temperature, it is not probable that any rearrangement occurs, and the reaction therefore affords conclusive evidence in favor of the formula $CH_3CO—NClC_5H_{11}$ as representing the constitution of this compound, and in favor of the corresponding structure for its analogues.

The Chlor- and Bromimido Ethers.

Ethylchlorimidobenzoate and Potassium Cyanide.—Ethylchlorimidobenzoate[1] does not react with potassium cyanide in absolute alcohol even on heating, but if water is added the reaction takes place spontaneously, potassium chloride crystallizes out, and the imido ether is regenerated. Eighteen grams of ethyl chlorimidobenzoate in aqueous alcohol were heated on a water-bath with 8 grams of potassium cyanide for an hour. After pouring the mixture into water, extracting with ligroin,

[1] Stieglitz: This JOURNAL, 18, 735 (1896).

and distilling *in vacuo*, an oil was obtained which contained 9.15 per cent nitrogen.

0.1170 gram substance required 9.5 cc. N_2 at 23° and 739 mm.

	Calculated for $C_9H_{11}NO$.	Found.
N	9.41	9.15

The oil gave a slight reaction with potassium iodide and was therefore ethyl benzimido ether still containing a little of the unchanged chlorine compound. Berg's reaction does not, then, take place with the chlorimido ethers.

Ethyl chlorimidobenzoate and zinc ethyl give benzonitril as the chief product though a little ethylamine appears to be formed. Eight grams ethyl chlorimidobenzoate were dissolved in twice the volume of ether and added slowly to 5 grams of zinc ethyl, a reflux apparatus with a stream of carbon dioxide being used. The ether was distilled off and water added to the cooled residue. On acidifying the mixture with hydrochloric acid, a light oil separated which was extracted with ether and was proved to be benzonitril by dissolving it in alcohol with a little ammonium hydroxide and passing in hydrogen sulphide. The thiamide formed melted at 114°, and at 115° when mixed with some thiamide prepared from benzonitril for comparison. The benzonitril recovered weighed 4.2 grams, *i. e.*, 94 per cent of the theoretical yield.

The acid solution was made alkaline and distilled into hydrochloric acid in a Liebig bulb. On evaporation a very small amount of a salt was obtained which gave the isocyanide odor with caustic potash and chloroform. This showed the presence of a primary amine. An analysis of 0.0162 gram of the platinum salt gave 35 per cent Pt (calculated for $(C_3H_5NH_2)_2PtCl_6$, 39 per cent).

Ethyl Chlorimido-m-nitrobenzoate, *m*-$NO_2C_6H_4C(NCl)OC_2H_5$. —This compound is easily made by dropping the hydrochloride of nitrobenzimido ethyl ester into an excess of sodium or calcium hypochlorite solution warmed to about 30°. On cooling,

[1] Lossen: Ann. Chem. (Liebig), **265**, 144 (1891); Tafel and Enoch: Ber. d. chem. Ges., **23**, 1550 (1890).

the chlorine compound becomes solid and can be picked off the surface with a spatula and recrystallized from warm alcohol or ligroin. It can be separated from any unchanged material by repeated extraction with ligroin.

0.2128 gram substance required 18.63 cc. N/10 thiosulphate.

	Calculated for $C_7H_5N_2OCl$.	Found.
N	15.50	15.52

It crystallizes in stellar groups of slender white needles and melts at 61° without decomposition, but when heated a little above this temperature it suddenly heats up and boils. On heating cautiously 5.5 grams of the compound, not absolutely dry, to the temperature required for decomposition, the chief product was *m*-nitrobenzamide, with a small amount of ethyl *m*-nitrobenzoate. Both compounds were identified by mixing them with the synthetic preparations and taking the melting-points. No derivatives of nitraniline could be found.

It was thought that stereoisomers of this compound might be prepared, but all efforts to obtain these were in vain. For example, ethyl chlorimidonitrobenzoate was dissolved in ligroin and a very little dry hydrogen chloride passed in. The hydrochloride of nitrobenzimido ester was precipitated. Of the amount taken, 80 per cent was recovered.

Attempts were made to substitute the chlorine attached to the nitrogen atom of ethyl chlorimidonitrobenzoate by treating it with dimethylaniline with the hope of forming a derivative of *p*-aminodimethyl aniline,[1] but without success. The two compounds were heated together in alcohol, in strong oxalic acid solution, in dilute and in concentrated sulphuric acid, and without any solvent, but on testing the product in each case, after saponification in acid solution, with hydrogen sulphide and ferric chloride, there was no trace of methylene blue, and it must be concluded that dimethylphenylenediamine was not formed even in the minutest quantity. Treating the chlorine compound with α-naphthol and an alkali also gave no evidence of the substitution of chlorine by a radical.[1]

[1] The apparently analogous chlorimides of quinone react in this way with anilines and phenols.

On heating the nitrobenzchlorimido ester in absolute alcohol it is not changed, but if a trace of water is present the benzoate is produced.

Nitrobenzchlorimido ester differs decidedly from the chloramides in being so stable. Alkalies do not cause the Beckmann rearrangement, nor even decompose it. Heating the ester for half an hour on the water-bath with an excess of 10 per cent potassium hydroxide does not affect it.

Ethyl Bromimido-m-nitrobenzoate, m-$NO_2C_6H_4C(NBr)OC_2H_5$. —The hydrochloride of nitrobenzimido ethyl ester is added to a cold solution of potassium hypobromite and the solution filtered at once. The precipitate is treated with ligroin, which dissolves the bromine compound and leaves the unchanged hydrochloride. By evaporation of the ligroin the bromimide crystallizes out in fine white needles which melt at 71°, turn brown at 120°, and give off a gas at 130°.

0.0338 gram substance required 2.15 cc. N/10 thiosulphate.

	Calculated for $C_9H_9O_2N_2Br$.	Found.
Br	29.27	27.30

The substance melts under water without decomposition. Dilute hydrochloric acid gives off bromine, and ethyl nitrobenzoate is formed. As with the corresponding chlorine compound, the attempt to attach the nitrogen atom to a benzene ring was not successful. Heating the bromimide with dimethylaniline and then with concentrated and dilute sulphuric acid, and then treating with hydrogen sulphide and ferric chloride gave no methylene blue.

Ethyl Imidonitrobenzoate and Hypoiodous Acid.—Since the chlorine and bromine derivatives of m-nitrobenzimido ethyl ester were so stable, it was thought possible that the corresponding iodine derivative might be prepared in the same way. The imido ester was treated with iodine and then with a solution of potassium hydroxide and with crushed ice. In another experiment a hypoiodite solution, made by dissolving iodine in cold potassium hydroxide solution, was used, but although in all cases the ether or ligroin extract gave a minute residue of white or yellowish crystals from which dilute

hydrochloric acid set free iodine, yet the desired iodine body was not definitely proved to exist, and it can probably be obtained, if at all, only from reagents when water is entirely excluded.

Ethyl Chlorimido-β-naphthoate, β-$C_{10}H_7C(NCl)OC_2H_5$.—The naphthimido ethyl ester was made by dissolving 15 grams of β-naphthonitril in 75 grams of ether and 8 grams of absolute alcohol, and passing in 10 grams of dry hydrogen chloride. The imido ester hydrochloride crystallizes out, on long standing, in plates. It decomposes with effervescence at 135° and forms the amide (m. p. 192°). Calcium hypochlorite solution has little effect on it in the cold, but if the solution is first heated to 60° or 70° the chlorine compound is readily formed, and can be filtered off on cooling and recrystallized from hot ligroin in beautiful stellar groups of needles and plates. It is very soluble in ether, from which it crystallizes in small, round nodules.

0.0525 gram substance required 4.48 cc. N/10 thiosulphate.

	Calculated for $C_{12}H_{12}ONCl$.	Found.
Cl	15.12	15.13

The chlorimidoester melts at 71° without decomposition, and only at 185° does it give off a gas with an agreeable odor, which burns with a green flame (ethyl chloride?). A gummy mass is left.

Ethyl chlorimido-β-naphthoate is not decomposed even by boiling with strong ammonium hydroxide. With sodium methylate it reverts to the nitril. On heating 1.5 grams with 10 cc. of anhydrous methyl alcohol containing sodium methylate prepared from 0.3 gram sodium, it reacted at once, the imido ether melting and dissolving. On pouring the mixture into cold water, naphthonitril was precipitated. Recrystallized from ligroin it melted at 66°, even when mixed with naphthonitril.

Berg's reaction does not take place with naphthchlorimide ester. Five grams of imido ester with one gram of potassium cyanide in absolute alcohol were warmed for half an hour on the water-bath. Most of the alcohol was then distilled off and

the residue extracted with ether. The part soluble in ether was distilled and found to be naphthonitril (m. p. 66°). The portion insoluble in ether (mostly potassium chloride) was dissolved in boiling water and some naphthoic acid crystallized out on cooling (m. p. 182°).

To 6 grams of the chlorimide in absolute ether were added 2.15 grams of zinc ethyl. There was no reaction at 0°, but when the mixture was allowed to come to the temperature of the room a slow effervescence began and continued for several hours. Filtering off the ether and evaporating it gave naphthonitril. On repeating the experiment with 20 grams of the chlorimide and 5.4 grams of zinc ethyl, there was a more rapid effervescence, but no precipitation of a zinc compound. On evaporating the solution in a vacuum, a salve-like mass was left which, treated with water, gave over 200 cc. of gas. The residue was extracted with ether and evaporated. A small portion of the product was recrystallized from ligroin and proved to be naphthonitril. In order to detect the presence of an amine, even in minute quantity, the remainder of the product was digested with sulphuric acid of varying concentration on a water-bath for several days. On pouring the solution into water, filtering off the unchanged nitril, making the filtrate alkaline with sodium hydroxide, and extracting it with ether, there was no evidence of an amine, from which it appears that zinc ethyl does not substitute ethyl for chlorine in acting on the chlorimide.

Ethyl Bromimido-β-Naphthoate, β-$C_{10}H_7C(NBr)OC_2H_5$.—This compound is made in the same way as the corresponding chlorine compound and resembles it in crystalline form and solubilities. Melting-point, 76°.5 to 77°.

0.1812 gram substance required 5.83 cc. N/10 thiosulphate.

	Calculated for $C_{13}H_{12}NOBr$.	Found.
Br	28.74	28.70

It crystallized from warm ligroin in pure white needles. It is remarkably stable. Boiling water and even sodium hydroxide solution attack it only very slowly. Standing over

night with strong ammonium hydroxide does not decompose it.

To Professor Stieglitz, not only for his skill in directing this work but also for his patience and kindness toward me personally, I feel very grateful.

Contributions from the Kent Chemical Laboratory of the University of Chicago.

THE RED AND THE YELLOW MERCURIC OXIDES AND THE MERCURIC OXYCHLORIDES.[1]

By Eugene P. Schoch.

According to Millon,[2] Roucher,[3] and Thümmel[4] the different mercuric oxychlorides exist in several isomeric modifications. It is stated that some of the isomers, on treatment with sodium hydroxide solution, give yellow mercuric oxide while the others give red. This would seem to indicate that there are two series of compounds, one of which is directly related to the yellow oxide, and the other to the red oxide. The two oxides, then, should be essentially different. Yet the results of recent investigations of the relations between the oxides contradict this conclusion. Since the published accounts of the several investigators of the oxychlorides are at variance on many points of detail, it seemed desirable to repeat critically all the methods of preparation of the oxychlorides, and to test the properties of these bodies with special reference to determining what oxide each yields when treated with sodium hydroxide solution. This problem was suggested to me by Professor Felix Lengfeld, formerly of the University of Chicago, and the work in this paper has been carried out under his direction.

It is evident that the solution of this problem requires a comparative study of the mercuric oxides. Hence, this paper is divided into two parts, presenting :

(1) A Study of the Mercuric Oxides.

(2) The Preparation and Properties of the Oxychlorides.

[1] The author's inaugural dissertation submitted to the faculties of the Graduate School of Arts, Literature, and Science of the University of Chicago, in candidacy for the degree of Doctor of Philosophy.

[2] Ann. chim. phys., (3), **18**, 372.

[3] *Ibid.*, (3), **27**, 353.

[4] Arch. Pharm., **227**, 589.

PART I.

A STUDY OF THE MERCURIC OXIDES.

It is well known that the red oxide of mercury, as ordinarily prepared by heating mercuric nitrate, is crystalline in its structure. Determinations of its crystal form were made by Nordenskjöld,[1] and by Descloizeaux,[2] who found that the crystals belonged to the monoclinic system. The structure of the yellow oxide, however, was an open question. Pelouze[3] and Millon[4] both state that it is amorphous, but beyond Millon's observation that under the microscope the yellow oxide presents the appearance of rounded globules, there is no record that either investigator subjected this substance to a critical examination. They considered the oxides as essentially different on account of the following differences in behavior. Pelouze points out that chlorine acts very slightly on the red oxide while it acts readily on the yellow oxide. Millon notes that the yellow oxide is converted by oxalic acid solution to white oxalate of mercury, and by alcoholic mercuric chloride solution to the black oxychloride, $HgCl_2,2HgO$, while the red oxide is scarcely affected by either reagent. Both authors admit that all of these differences are quantitative rather than qualitative. It is easily found by trial that the differences become less and less as the red oxide is more finely powdered. Concerning the action of oxalic acid, this conclusion has been confirmed recently by Koster and Stork.[5] Hence these differences in the behavior of the two oxides pointed out by Millon and Roucher do not appear to give ground enough whereon to base the conclusion that the oxides are essentially different.

In contrast to the older idea, that the yellow oxide is amorphous, are the results of recent investigations which seemed to show that the two oxides are identical and differ only in the size of the particles. Ostwald[6] found that both

[1] Pogg. Ann., **114**, 612.
[2] Ann. chim. phys., (4), **20**, 210.
[3] Compt. rend., **16**, 50.
[4] *Loc. cit.*
[5] Rec. trav. chim. Pays-Bas., **20**, 394.
[6] Ztschr. phys. Chem., **18**, 159.

oxides have very nearly the same solubility in normal solutions of potassium bromide, potassium iodide, and of sodium thiosulphate, and that a cell "mercury-yellow oxide-potassium hydroxide solution-red oxide-mercury" gave no appreciable electromotive force. This latter would show that the two oxides have the same solubility. However, Cohen[1] measured the electromotive force of a cell arranged in the same way with a much more delicate electrometer, and concluded from his results that at ordinary temperatures the yellow oxide is more soluble than the red and hence, that they could not be identical. In answer to this, Ostwald[2] showed that the solubility of a sparingly soluble powder varies appreciably with the size of the particles, a fact which has received further confirmation by Hulett,[3] and appears to have a secure theoretical foundation. By grinding red oxide of mercury very fine, Ostwald found that its solubility in normal potassium bromide and the other solutions referred to can be made equal to the solubility of the yellow oxide, and even to exceed it. He concludes that the two oxides are identical.

With the exception of some bare statements to the effect that the yellow oxide, on heating, changes to the red,[4] and that it dissociates at a lower temperature,[5] the foregoing is all that has come to my notice which in any way bears on the subject.

My own results may be summarized as follows:

(*a*) Yellow oxide, when precipitated, washed, and dried at the ordinary temperature, is crystalline, but shows a form entirely different from that in which the red oxide crystallizes. Under a microscope which magnifies 1,000 to 1,200 diameters the yellow oxide is seen to be in the form of square tablets.

(*b*) The crystals of the yellow oxide grow when allowed to remain, at the ordinary temperature, in contact with the precipitation mixture, or with sodium or potassium chloride solutions. At the same time the color of the mass changes from a pale-yellow to an orange, and after some weeks to a decidedly

[1] Ztschr. phys. Chem., **34**, 69.
[2] *Ibid.*, **34**, 495.
[3] *Ibid.*, **37**, 385.
[4] Carnelley and Walker: J. Chem Soc. (London), **53**, 59.
[5] Wallace: Chem. Gaz., 1858, p. 345.

reddish tint. It appears from this that the square tablets are stable at the ordinary temperature.

(*c*) When the crystals of the yellow oxide are boiled in aqueous solutions of salts, they change to the prismatic form of red oxide. The change takes place very completely when a little of the powder is suspended in a 10 per cent (or stronger) solution of sodium or potassium bromide or chloride and the mixture boiled for an hour. The color of the resulting mass may or may not be deeper, depending upon the relative sizes of the crystals before and after change. Samples precipitated hot show a number of prismatic crystals.

(*d*) On heating dry samples of the yellow oxide to temperatures from 250° C. to 600° C., for periods of eight to twenty-four hours, the crystals changed to the prismatic forms of the red. In this connection it was found that yellow oxide changed in color to a deep-orange or yellowish-red, while samples of red oxide which had been ground fine till they were yellow in appearance, did not change, although heated to the same temperature and for the same length of time. The microscope revealed the fact that the samples of red oxide were still made up of the same fragments of prismatic crystals of which they consisted before heating, while the samples of yellow oxide showed a complete change of form to the prismatic.

It is evident that, to some extent, the color of the mass does not enable us to decide whether a sample is the yellow or the red oxide. I have obtained samples with square tabular crystals (yellow) that show a deeper color than many samples with prismatic crystals (red).

(*e*) The prismatic crystals obtained according to (*c*) and (*d*) are identical with the regular red oxide crystals. Miss H. Whitten, of the University of Texas, examined these samples and gave me the following statement of her conclusion. "All show decidedly prismatic forms, singly, or in aggregates. From the appearance of prism and pinacoidal faces shown by all the forms examined, I would say they are typical monoclinic prisms. $<\beta$ was not (could not be) measured, but appeared constant in all the samples."

It appears, then, that mercuric oxide exists in two crystalline forms: one, square tabular crystals, is formed by precipitation at the ordinary temperature, and changes to the other form when exposed to higher temperatures; the other, monoclinic prisms, results in all preparations made at temperatures above the ordinary.

In considering the question of their relation, the first possibility that presents itself is that the yellow oxide is an hydroxide. Though this point had been carefully investigated by Siewert,[1] it appeared desirable to study it again, because Carnelley and Walker[2] announced a contrary result. The experimental results, given elsewhere, agree perfectly with Siewert's and show that the yellow oxide is not a hydrate and that the two oxides have the same composition.

Different crystal forms of the same substance usually have different densities, and since no record of determinations of the density of the yellow oxide could be found, comparative determinations with both oxides were made. However, it soon became evident that the difference in density, if any exists, is very small. The amount of time necessary for accurate density determinations rendered it undesirable to continue this work at that time.

Since at higher temperatures the yellow oxide changes to the red, the dissociation pressure of the yellow should be greater than that of the red. This has been found to be the case. At 300° to 320° C. the dissociation pressure of the yellow is 760 mm. and over, while that of the most finely powdered red oxide does not exceed 400 mm. Of course, the yellow oxide is soon converted to the red. After an hour's heating at 380° the yellow exerted a much smaller tension—one corresponding to the red.

Other relations between the oxides, such as solubility, relation of specific heats, etc., have not been studied so far, but are to be determined by future work. It is probable that the solubility of the yellow oxide at and below the ordinary temperature is less than that of the red oxide, the size of the particles of both samples being the same. This is to be expected from

[1] Ann. Chem. (Liebig), **125**, 226.
[2] *Loc. cit.*

the fact that the crystals of the yellow became larger, as shown in (*b*) above, and also from the fact found by Ostwald that the solubility, in normal potassium bromide solution, of red oxide finely ground with garnets exceeded that of the yellow oxide.

Furthermore, it follows that at low temperatures the prismatic crystals should change to the square, tabular, and that there should be a definite transition temperature for these two forms.

In the light of the information just presented the oxides obtained by treating the mercuric oxychlorides with sodium hydroxide present nothing new or peculiar. I found that all the ten oxychlorides I have prepared (see second part of this paper) when treated with sodium hydroxide at the ordinary temperature, yield an oxide that contains square tabular crystals. In some cases the form was not well defined, but it certainly was not prismatic. However, when it became necessary to heat the mixture in order to decompose the oxychloride thoroughly (*e. g.*, black trimercurdioxychloride) prismatic crystals were obtained. These results agree perfectly with the preceding.

It is probable that Millon, Roucher, and Thümmel took the colors of the masses as a criterion. I have already pointed out that the color does not enable us to decide, and I found my view corroborated in this case : the difference in the colors of the oxides obtained from the oxychlorides is due to the sizes and irregularities of the particles, and in some cases, to the presence of nuclei of undecomposed oxychloride.

Preparation of Mercuric Oxide Showing Square Tabular Crystals.

Cold saturated mercuric chloride solution was added to sodium hydroxide solutions of concentrations ranging from 2 to 30 per cent. The ratio between the amounts of mercuric chloride and sodium hydroxide never exceeded that of 1 molecule of mercuric chloride to 10 of sodium hydroxide. For the most concentrated sodium hydroxide solutions the relative quantity of mercuric chloride added was much less ; the quan-

tities were in the ratio of 1 molecule of mercuric chloride to 20 of sodium hydroxide. The addition of more mercuric chloride solution would have made the mixtures too dilute. The mixtures were allowed to stand from four to six weeks with occasional stirring. In all except the most concentrated, the yellow precipitates soon turned orange, the color deepening day by day for about two weeks. The maximum change was observed with the 10 per cent sodium hydroxide mixture, a deep orange or reddish-yellow color being produced.

Some precipitates, prepared as above, were washed by decantation immediately after precipitation, while they were still pale-yellow, and then they were allowed to stand, part under pure water, part under 10 per cent sodium hydroxide solution. No perceptible change took place. When sodium chloride was added to the solution the change began.

After four to six weeks, the precipitates were washed, dried, and examined under the microscope. The following description, based upon an examination of ten samples, was given me by Mr. R. D. George, of the Department of Geology of the University of Chicago:

"The samples show a considerable number of small tabular crystals of apparently equal lateral axis. The exact outline of the crystals could not be determined on account of the light interference. In polarized light the crystals showed distinct double refraction, giving a pale yellowish-green interference color. The existence of double refraction was further confirmed by the use of the selenite plate."

"Besides these small crystals there were others of larger size, having angles differing by a few degrees from a right angle. These presented the appearance of skeleton crystals. The centers presented much less obstruction to the passage of light than the borders did. The shape of the less opaque central part could not be determined, but its outline appeared rounded and not parallel with that of the crystal as a whole. This apparent difference of form may have resulted from light interference, or from the presence of a greater thickness of the crystal substance at the angles."

From the microscopic examination it also follows that the

change in color noted above was due to an enlargement of the crystal grains. This probably takes place as usual: the smaller grains dissolve and the oxide crystallizes out again on the surface of the larger crystals. Hence, anything that increases the solubility of the mercuric oxides hastens the change. In accordance with this I found that water or sodium hydroxide solution free from chloride had no perceptible effect, while on the addition of sodium chloride to both a change in color was immediately noticed. As is well known, mercuric oxide is but very slightly soluble in water, and probably not much more soluble in sodium hydroxide solution, but it is much more soluble in solutions of many salts. While I tried sodium and potassium chloride only, it is to be expected that other salts, such as sodium nitrate or sulphate, would have a somewhat similar effect.

Experiments Showing that the Crystals Obtained by the Action of Hot Aqueous Solutions on Yellow Mercuric Oxide are Prismatic.

1. One hundred cc. of hot mercuric chloride solution (50 grams of mercuric chloride to 100 cc. water) were added, gradually, to 500 cc. of hot potassium hydroxide solution (50 grams of potassium hydroxide to 100 cc. water). The mixture was boiled for five hours in a flask with a reflux condenser. Then the precipitate was allowed to settle, was washed by decantation, and finally spread on porous plates to dry. The microscopic examination showed that most of the particles were in the form of prismatic crystals. Other forms could not be clearly recognized.

2. An excess of hot potassium hydroxide solution was added to 250 cc. of hot mercuric chloride solution, both of the same concentrations as in 1. The mixture was boiled for five hours in a flask with a reflux condenser, then the precipitate was washed and dried. The mass did not show any well defined crystals of any sort. It should be noted, in passing, that the quantity of precipitate relative to the same volume of solution was at least six times as large in this case as in number 1. This may account for the absence of well formed crystals.

3. Mercuric oxide was prepared by Bosetti's[1] method, adding hot barium hydroxide solution to a hot concentrated mercuric chloride solution. The oxide obtained showed some well-defined, prismatic crystals, though on the whole it was decidedly impure.

4. One hundred grams of yellow oxide were suspended in 500 cc. of potassium hydroxide solution (same concentration as before) and the mixture boiled for five hours. The oxide was then washed and dried. Under the microscope prismatic crystals could not be clearly identified.

5. Thirty-five grams of the yellow oxide as in 4 were boiled for five hours in a solution of 125 grams of potassium chloride, 125 grams of potassium hydroxide, and 400 cc. of water. The oxide was then washed, dried, and examined. It was made up of well-formed, prismatic crystals.

6. Twenty grams of the same sample of yellow oxide were boiled for two hours in a solution of 220 grams of potassium chloride in 500 cc. of water previously saturated with mercuric oxide. On examination this sample showed large prismatic crystals.

Experiments 1 to 3 differ from the others in this respect: the oxide was first formed in the mixture, while in experiments 4 to 6 yellow oxide was added as such.

The same considerations which suggested themselves in connection with the enlargement of the crystal grain of the yellow oxide find application here. The largest and most perfect crystals were obtained by the action of the solution which dissolved the largest amount of the oxide. In experiments 2 and 4 prismatic crystals were not formed, probably because in 2 the volume of the solution was inadequate and in 4 the solubility of the oxide was slight.

Determination of Water in the Yellow Oxide.

Siewert[2] had found that yellow mercuric oxide, dried carefully over sulphuric acid, contained only 0.52 per cent of water as obtained by absorption in a calcium chloride tube. Carnelley and Walker merely heated mercuric oxide (air-

[1] Pharm. Ztg., 38, 471.
[2] *Loc. cit.*

dried for five months) in a crucible and determined the loss in weight at different temperatures. They found a loss of 0.50 per cent up to 100° C. and 8.5 per cent up to 175°. At this temperature they report complete dehydration, and, at temperatures beyond these, incipient decomposition. The grounds for deciding that up to this point there is dehydration and not decomposition are not clearly stated: perhaps they thought decomposition could not be extensive since, according to Myers, the dissociation pressure of mercuric oxide at 175° is very low. However, I had observed that yellow mercuric oxide decomposes appreciably at that temperature, hence I thought that the loss due to heating the oxide above 100° may be due entirely to decomposition.

Yellow oxide was freshly prepared from mercuric chloride with an excess of sodium hydroxide, samples (*a*) and (*b*), by pouring the hydroxide into the chloride solutions; sample (*c*) by reversing the procedure. The samples were washed nine times by decantation with large quantities of water, and were tested for chlorine by dissolving them in nitric acid, precipitating the mercury as the sulphide, boiling the filtrate till free from hydrogen sulphide, and adding silver nitrate. Chlorine was absent. They were dried in a vacuum desiccator for four days.

The samples were heated in an air-bath at 80° for four hours, to constant weight.

(*a*) 10.7447 grams lost 0.0370 = 0.34 per cent.
(*b*) 20.0900 " " 0.0500 = 0.24 "
(*c*) 21.0526 " " 0.0568 = 0.27 "

These samples were then placed in U-tubes, through which was passed a slow current of dry air. The tubes were heated in a bath of concentrated sulphuric acid. The upper parts of the U-tubes were kept cool. The current of air was drawn through calcium chloride absorption tubes. The bath was gradually heated up to 198° in the course of four hours.

(*a*) 10.7143 grams lost 0.0257 gram = 0.23 per cent; its calcium chloride tube gained 0.0371 gram = 0.34 per cent.

(*b*) 11.3273 grams lost 0.0121 gram = 0.16 per cent; its calcium chloride tube gained 0.0273 gram = 0.24 per cent.

(*c*) 10.8265 grams lost 0.0217 gram = 0.20 per cent; its calcium chloride tube gained 0.0356 gram = 0.33 per cent.

Considerable decomposition had taken place in all the samples, as shown by the mercury deposited in the cool parts of the U-tubes. To determine the amount, another portion of sample (*c*) was heated in a dish in an air-bath to 175° for three hours—10.0216 grams lost 0.8117 gram = 8.1 per cent.

Two other samples prepared as above were analyzed for mercury by electrolysis.

I. 0.4019 gram substance gave 0.37135 gram Hg.

II. 0.36985 gram substance gave 0.34125 gram Hg.

	Calculated for HgO.	Found. I.	II.
Hg	92.6	92.4	92.3

An average of about 0.50 per cent of water was found in the yellow oxide, agreeing with Siewert's result. The hydrate $Hg(OH)_2$ requires 7.68 per cent. The loss in weight that Carnelley and Walker report as water was most likely due to decomposition.

Determination of the Densities of the Oxides.

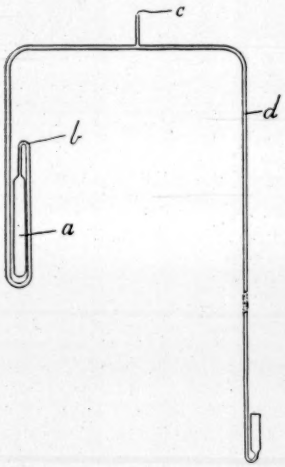
The densities were determined in absolute alcohol, and the temperature noted to 0°.1. The air was removed by placing the flask containing the oxide with enough alcohol to cover it, in a vacuum desiccator; under low pressure the alcohol boiled at the ordinary temperature, thus aiding the removal of the air. No constant temperature room and similar refinements were employed, hence the experimental error is relatively large, especially with substances of such great density.

Red oxide, Kahlbaum	27°.5	11.08
Same, finely ground	27°.5	11.11
Yellow oxide, my own preparation	27°.5	11.03
Yellow oxide, Kahlbaum	28°.5	11.08

Determination of Dissociation Tension.

In attempting to measure the dissociation tension of the mercuric oxides, one is confronted by a peculiar difficulty: since the manometer with which the apparatus is connected must be kept cool, the mercury condenses at this point, and

constantly disappears from the vapor in the hot part of the apparatus. I soon found by trial that equilibrium cannot be maintained even for ten or fifteen minutes unless the distilling of the mercury is prevented or minimized. After trying various forms of apparatus, I found the following to work satisfactorily (see sketch): The oxide was put into a tube 1 cm.



in diameter and 20 cm. in length, closed at its lower end and at the upper fused to a capillary tube about 1 mm. in diameter. This capillary tube was bent 10 cm. from the joint so that it extended downward close to the wide tube. Then it was bent to pass around the lower end and up along the tube again. Finally, 10 cm. above the first bend it was bent at a right angle and extended out some 30 cm. from the heating oven, where the tube was bent downwards to serve as a manometer. The wide tube with the capillary tube around it was placed as deep into a well-closed air-bath as the exit tube would permit. By this means the distillation of the mercury

was retarded so that equilibrium was not sensibly disturbed by this cause. In testing the apparatus I found that a sample of red oxide kept at 400° for two hours did not vary more than 3 to 5 mm. from its mean pressure (182 mm.). At the end of the time it registered 184 mm.

The manometer consisted of a continuation of the capillary tube 32 inches in length, to the lower end of which was fused a short piece of wide tubing, bent upwards, to serve as a reservoir for mercury. This reservoir was open to the air, and, from it, the mercury was drawn into the manometer tube as the apparatus was exhausted.

In every case the manometer was filled so as to avoid air bubbles on the tube, all the moisture was carefully removed from the apparatus, and the air exhausted to 1 mm. or less, as measured by another manometer on the pump.

The samples were dried for four days in a vacuum desiccator over phosphorus pentoxide. To insure the absence of mercurous oxide, the samples were heated above 100° by means of a boiling salt solution (b. p. 108°) while the apparatus was being exhausted (ten to fifteen minutes). Twenty to twenty-five grams of oxide were placed in each apparatus.

Trial experiments showed that the ground red oxide exerts a greater tension than the coarse oxide, hence, I used finely ground red oxide in comparing its tension with that of yellow oxide.

I had also found that yellow oxide shows its own proper tension only for a very short time when first heated. For instance, a sample of Kahlbaum's yellow oxide, when first heated to 320°, showed a pressure of 660 mm. It was then allowed to cool, having been hot for less than two hours altogether. Then it was shaken up, exhausted again, and heated to 350°, when it showed a tension of 200 mm., while a sample of coarse red oxide heated with it showed a tension of 160 mm. Hence I decided to heat the samples rapidly to a certain temperature and to take the first reading that the yellow oxide gives.

For the final trial the following samples were heated together:

1. Red oxide, finely ground.
2. Merck's best yellow oxide.
3. Yellow oxide, my own preparation, well crystallized.

These were heated rapidly to 310°. All samples reached their maximum pressures quickly. Number 3 exerted a pressure of 760 mm., and evolved several bubbles of gas through the manometer. Number 2 exerted a pressure of 730 mm., and, after half an hour, showed a slight decrease of 10 to 15 mm. No 1 soon reached 370 mm. and after an hour stood at 375 mm.

PART II.

PREPARATION AND PROPERTIES OF THE OXYCHLORIDES OF MERCURY.

There are three distinct methods of preparing oxychlorides of mercury:

(1) By the action of alkali bicarbonates on mercuric chloride solutions.

(2) By the action of mercuric oxide, red or yellow, on mercuric chloride solutions.

(3) By the fusion of mercuric oxide with mercuric chloride.

The first method was studied by Millon.[1] His work is both accurate and exhaustive, and little of note has been added since.

Roucher[2] investigated the second method. Many of the compounds he reported were afterwards found to be mixtures.

Thümmel[3] repeated the work of both Millon and Roucher. He revised the latter's results and gave definite directions for the preparation of all known oxychlorides by wet methods. In preparing my own samples, I subjected Thümmel's directions to a critical review, and found them correct with the exception of the modifications and differences presented farther on.

The third method is given by André.[4] He fused together

[1] *Loc. cit.*
[2] *Loc. cit.*
[3] *Loc. cit.*
[4] *Loc. cit.*

mercuric oxide and mercuric chloride in nearly stoichiometric proportions. Unlike Thümmel's directions, André's could not be depended upon. He claims to have prepared four oxychlorides, but probably none were pure, and hence the whole method was submitted to investigation.

I propose to name the oxychlorides by indicating the number of mercury and oxygen atoms, thus:

$2HgCl_2,HgO$, trimercuroxychloride;

$HgCl_2,2HgO$, trimercurdioxychloride, etc.

I obtained ten oxychlorides, one $2HgCl_2,HgO$, trimercuroxychloride, and three isomers of each of the following:

$HgCl_2,2HgO$, trimercurdioxychloride;

$HgCl_2,3HgO$, tetramercurtrioxychloride;

$HgCl_2,4HgO$, pentamercurtetroxychloride.

Dimercuroxychloride, $HgCl_2,HgO$, could not be obtained.

All the compounds were analyzed. For the determination of chlorine two methods were employed. In one the substance was heated with pure calcium oxide in a piece of combustion tubing to expel the mercury. The mass was dissolved in dilute nitric acid, and the chlorine determined as usual. This was tested by five check analyses, agreeing within 0.2 per cent. In the second method, the oxychloride was dissolved in acetic acid, and a solution of 10 grams of sodium acetate with an excess of silver nitrate added, the mixture heated to 70° with stirring, and then allowed to cool in the dark. Two trial determinations agreed to 0.1 per cent. The mercury was determined by electrolysis.

I determined the densities of all the oxychlorides, proceeding as for the oxides (see page 329).

I will discuss individually the oxychlorides prepared by wet methods as far as I have noticed anything new about them, and afterwards present an investigation of the fusion of mercuric chloride with mercuric oxide.

Trimercuroxychloride, $2HgCl_2,HgO$.—For the preparation of this substance Thümmel's directions were inadequate. An absolutely pure sample of this substance could not be obtained

by using red oxide or commercial samples of yellow oxide, even with the following procedure, though this yielded better results than any other: A sample of red and another of commercial yellow oxide were moistened, ground in a mortar, and added slowly, with stirring, to moist mercuric chloride (1 part of oxide to 10 of chloride and 5 of water). The masses were put in glass-stoppered bottles and shaken for four days in a thermostat at 65°. The substances still showed particles of unconverted oxide, and were easily decomposed by the light. The analysis of a sample prepared from red oxide showed 18.01 per cent chlorine; that from commercial yellow oxide 18.2 per cent (theory, 18.69 per cent).

However, a pure sample was obtained by using moist yellow oxide freshly precipitated at the ordinary temperature. This was added gradually to moist mercuric chloride in the proportions given above. The mixture was warmed in a water-bath with occasional stirring, the liquid decanted, the mass dried, and then washed with absolute ether to remove all excess of mercuric chloride. This compound has a pale straw-yellow color.

I. 0.5242 gram substance gave 0.3901 gram AgCl.

II. 0.5278 gram substance gave 0.3969 gram AgCl.

	Calculated for $2HgCl_2.HgO$.	Found. I.	II.
Cl	18.69	18.4	18.56

Another method that yielded a pure compound was the following: 25 to 30 grams of mercuric chloride were dissolved in 100 cc. of boiling water and as much finely ground mercuric oxide was added as the solution would dissolve. The mixture was then cooled and the crystals separating between 60° and 40° were collected, dried, and washed with ether. The samples showed relatively large crystals of isometric rhombic dodecahedra.

0.4526 gram substance gave 0.3376 gram AgCl.

0.4718 gram substance gave 0.3738 gram Hg.

	Calculated for $2HgCl_2.HgO$.	Found.
Cl	18.69	18.47
Hg	79.20	79.00

Roucher claimed that among the crystals separated below 40° a less basic oxychloride can be found, but I noted nothing that would indicate the existence of such a compound.

I found the density of trimercuroxychloride to be 6.42.

Trimercurdioxychloride, $HgCl_2,2HgO$.—The red and the black modifications of trimercurdioxychloride are perhaps the most interesting of these bodies, because they, more than any of the other oxychlorides, present clearly a case of isomerism, which is otherwise so rare among inorganic compounds. The two sets of crystals have different densities, and show a notably different behavior with reagents. For example, both alkali carbonate and alkali chloride solutions readily act upon the red modification in the cold, while they do not affect the black even on boiling.

I made a comparative study of the methods of preparation of these isomers, and noted that the conditions for the formation of these compounds are essentially identical, except that for the preparation of the red modification the liquid must be slightly acid, while for the black it must be slightly alkaline. This may be seen from the following statement of facts.

Under the following conditions only the black modification is formed :

(*a*) By the action of sodium acetate on mercuric chloride solution.[1] The mixture has an alkaline reaction towards litmus. Black trimercurdioxychloride crystallizes out very slowly.

(*b*) By the addition of very small quantities of potassium bicarbonate solution, at intervals of half a day or a day, to mercuric chloride solution. The amount of the potassium bicarbonate added should be so slight that no precipitate will be produced. As the carbon dioxide escapes, and the solution becomes faintly alkaline, black trimercurdioxychloride crystallizes out slowly.

(*c*) By shaking an excess of mercuric oxide with a very dilute solution of mercuric chloride. Here the liquid is under the predominating influence of the mercuric oxide. This latter is an essential point, and may be noted again when mer-

[1] Volhard : Ann. Chem. (Liebig), 253, 252.

curic chloride is poured upon a thick layer of mercuric oxide without disturbing the latter, and the whole allowed to remain at rest. Black trimercurdioxychloride does not form in the top layer of the oxide, but forms in lower layers.

(*d*) By the action of water on trimercuroxychloride.

The method usually employed to obtain the black trimercurdioxychloride in larger quantity—adding mercuric oxide gradually to a boiling solution of mercuric chloride—probably depends on the action shown in (*d*) and is complicated by the fact that the oxide and chloride first form trimercuroxychloride.

Under the following conditions only the red modification is formed:

(*e*) By the action of marble on mercuric chloride solution.[1] The oxychloride forms on the bottom and the sides of the vessel—not on the marble. The solution is faintly acid to litmus.

(*f*) By mixing solutions of mercuric chloride and potassium bicarbonate, in the proportion of 8 molecules of mercuric chloride to 11 molecules of potassium bicarbonate. At the beginning the mixture is alkaline, and the action results in the formation of a yellow oxychloride—probably tetramercurtrioxychloride, which is more basic than the one under discussion—but the alkalinity is soon overcome by the acid liberated, and now the red trimercurdioxychloride is formed. Of course, carbonic acid escapes in large amount, and in the end the liquid is alkaline, because in the equilibrium condition of potassium chloride and mercuric oxide the liquid must be alkaline.

(*g*) By the addition of alcohol to mercuric chloride solutions which have been treated with mercuric oxide. In this case the solution is acid to litmus.

Methods (*a*) and (*b*) for the black are comparable to (*e*) and (*f*) for the red compound, and (*c*) is comparable to (*g*). All of these support my observations that the only difference in the preparation of these isomers is the acidity or alkalinity of the liquid. There is no method for the red corresponding to method (*d*) for the black compound.

[1] Arctowski: Ztschr. anorg. Chem., 9, 178.

Thümmel converted the red into the black oxychloride by heating: I could not bring about this conversion by any means. As I obtained the red it does not form square plates, as Thümmel found, but short hexagonal prisms (almost plates) with a pyramid on each end.

I found the density of the red modification to be 8.16 and that of the black 8.53.

Tetramercurtrioxychloride, $HgCl_2,3HgO$.—This, like the preceding, cannot be obtained pure by following Thümmel's directions, that is, using red oxide or commercial yellow oxide of mercury, even when prepared by grinding the oxides moist, adding them to the mercuric chloride in cylinders, and mixing by slowly inverting the cylinders again and again for several hours. When thus prepared, a sample from the red oxide showed 7.58 per cent chlorine, and one from the yellow 7.63 per cent. This seems to be sufficiently near the per cent required by theory (7.7 per cent), but even the trace of oxide in these samples renders the preparation unstable. The compound is obtained pure by using freshly precipitated oxide and adding it to cold saturated mercuric chloride solution so that the relative quantities do not exceed the proportion of 2 molecules of mercuric chloride to 1 molecule of mercuric oxide. The mixture is gently shaken after each addition. After standing about ten minutes the liquid is decanted, the mass dried on porous plates, and then washed with absolute ether.

I. 0.4216 gram substance gave 0.1326 gram AgCl.
II. 0.5823 gram substance gave 0.1818 gram AgCl.
III. 0.3107 gram substance gave 0.2697 gram Hg.

	Calculated for $HgCl_2,3HgO$.	Found. I.	II.	III.
Cl	7.70	7.78	7.72	....
Hg	87.08	....	....	86.80

As thus prepared, the substance forms distinct prisms. It is not changed by (*a*) light, (*b*) heating dry to 110°, or (*c*) boiling with a 7 per cent mercuric chloride solution. With excess of moist mercuric chloride it changes to $2HgCl_2,HgO$ without passing through any intermediate compound, such as

$HgCl_2.2HgO$. Heated with water, yellow tablets of pentamercurtetroxychloride, $HgCl_2.4HgO$, are formed. These observations are contrary to those of Thümmel, who found that the substance, when heated dry, blackens below 180°, is unstable in the light, heated with water gives black $HgCl_2.2HgO$ and brown $HgCl_2.4HgO$, and with mercuric chloride solution gives black $HgCl_2.2HgO$. However, I found that impure samples behaved according to Thümmel's observations.

The density of this modification of tetramercurtrioxychloride was found to be 7.93. Besides this modification of tetramercurtrioxychloride, there are two others: One, brick-red, amorphous, was prepared according to Voit's[1] directions; the other, yellow plates, was prepared according to Millon.[2] I noted nothing particular about either. Since they could not be isolated without decomposition, their densities were not determined.

Pentamercurtetroxychloride, $HgCl_2.4HgO$.—(*a*) Yellow hexagonal plates. (*b*) Brown amorphous.

Both of these modifications are easily obtained pure by following Thümmel's[3] directions. I found the density of (*a*) to be 9.008, and of (*b*) to be 9.050.

Investigation of the Fusion of Mercuric Chloride with Mercuric Oxide.

Mercuric chloride and mercuric oxide, in various proportions, were carefully ground together, put into sealed tubes, and heated to 300° for six to eight hours. The resulting masses were ground, examined microscopically, and then treated with ether, first in a Soxhlet extraction apparatus and then by washing by decantation until the wash ether left no residue upon evaporation. Then the substances were examined again microscopically, and if apparently homogeneous, they were analyzed for chlorine and mercury. The same compound,—clear wine-red crystals of $HgCl_2.2HgO$,—was obtained in each of the following:

[1] Ann. Chem. (Liebig), **104**, 351.
[2] Ann. chim. phys., (3), **18**, 333.
[3] *Loc. cit.*

I. $10HgCl_2 + HgO$, red, heated six hours.
II. $2HgCl_2 + HgO$, red, heated six hours.
III. $HgCl_2 + HgO$, red, heated six hours.
IV. $HgCl_2 + 2HgO$, red, heated six hours.
V. $HgCl_2 + HgO$, red, heated three hours.
VI. $HgCl_2 + HgO$, with a few drops of water, heated six hours.
VII. $10HgCl_2 + HgO$, yellow, heated six hours.
VIII. $HgCl_2 + HgO$, yellow, heated six hours.

	Calculated for $HgCl_2,2HgO$.	Found.							
		I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Cl	10.07	10.3	9.90	9.99	10.05	9.90	10.14	10.08	9.97
Hg	85.38	85.38	...	85.08	....	85.16	....	....	....

Hence an excess of mercuric chloride over that required for the product $HgCl_2,2HgO$ always remained uncombined.

On the other hand, mixtures containing more oxide than is required for $HgCl_2,HgO$ resulted in the following:

(*a*) $HgCl_2 + 4HgO$, a dark-brown mass of pentamercurtetroxychloride not well crystallized.

(*b*) $HgCl_2 + 3HgO$, wine-red crystals of trimercurdioxychloride, mixed with brownish-yellow crystals, which were found to be pentamercurtetroxychloride.

(*c*) $HgCl_2 + 6HgO$, mixture of pentamercurtetroxychloride crystals with free oxide.

There are no methods known by which such mixtures as these may be separated, hence the microscope was the only means of examining them. The oxychloride $HgCl_2,4HgO$ was obtained pure for recognition and analysis by heating a mixture of $HgO + 2HgCl_2$ in a tube and keeping the empty end cooler than the other. Mercuric chloride distilled to this end, and in the other remained a homogeneous mass of black, shining crystals—hexagonal plates of a pale slate-blue (reddish-brown or yellow, according to thickness) color, which gave upon analysis:

I. 0.9804 gram substance gave 0.2557 gram AgCl.
II. 1.0326 grams substance gave 0.2693 gram AgCl.
III. 0.4226 gram substance gave 0.3722 gram Hg.

	Calculated for $HgCl_2,4HgO$.	Found. I.	II.
Cl	6.24	6.45	6.32
Hg	88.13	88.07	....

Hence, an excess of mercuric oxide over that required for the product $HgCl_2,4HgO$ remained uncombined.

In these preparations only two distinct oxychlorides were formed:

$$HgCl_2,2HgO \qquad \text{and} \qquad HgCl_2,4HgO.$$

The other compounds André gives were probably mixtures.

The density of this form of trimercurdioxychloride is found to be 8.43 and of the pentamercurtetroxychloride 9.107.

The foregoing paper was finished several months ago, but I was delayed in sending it off for publication. In the meanwhile an article by Schlick[1] has appeared which I wish to note briefly.

The author's results, valuable as they are, do not support his conclusion as to the identity of the oxides when the facts presented in this paper are considered. In the first place, the only criterion Schlick used for distinguishing between the oxides was the color, which I have found to be unreliable; in the second place, it was to be expected, or at least quite likely that under the circumstances the solubilities of both forms appear to be the same because the form unstable at the temperature of the experiment is converted to the stable form.

In conclusion, I wish to thank Professor Felix Lengfeld for the kind assistance and valuable suggestions he has given me in the prosecution of this work.

I also wish to thank Miss H. Whitten and Mr. R. D. George for the favors shown me in the microscopical examinations of samples of the mercuric oxides.

CHICAGO, August 1, 1902.

[1] Ztschr. phys. Chem., **42**, 155.

THE DETERMINATION OF MOLECULAR WEIGHTS.

By H. C. Biddle.

The influence of a dissolved substance upon the vapor-pressure of its solvent was a subject of study as early as the time of Gay-Lussac. The first generalization of much importance, however, was made by Wüllner[1] in 1858. This investigator showed that in aqueous solutions of non-volatile substances, the lowering of the vapor-pressure was roughly proportional to the quantity of substance dissolved. In the investigations of Wüllner and of those immediately following him, attention was directed largely to the study of salt solutions,[2] consequently more than a quarter of a century elapsed before a clear insight into the phenomena of vapor-tension was gained. The extension of the study of vapor-pressures to solutions other than aqueous, we owe chiefly to Raoult.[3] This investigator had noted the close relation existing between the diminution of the vapor-pressure of a solution, the lowering of its freezing-point, and the number of molecules of the dissolved substance, and was led by these considerations to study the vapor-pressures of ethereal solutions. His work gave definition to the entire subject, and is undoubtedly the most important that has ever been done on the vapor-tension of solutions.[4]

Among his results the following are of particular consequence: The relative vapor-pressure, $\frac{f'}{f}$, between 0° and 22° is independent of the temperature; the relative lowering of the vapor-pressure, $\frac{f-f'}{f}$, is proportional to the molecular concentration; the depression, $f-f'$, produced in a solution of a non-volatile substance, is independent of the nature of that substance; and the lowerings of vapor-pressure in various

[1] Pogg. Ann., **103**, 529 (1858); **105**, 85 (1858); **110**, 564 (1860).

[2] Panchon: Compt. rend., **89**, 752 (1879); Tammann: Wied. Ann., **24**, 523 (1885); Emden; *Ibid*, **31**, 145 (1887); etc.

[3] Compt. rend., **103**, 1125 (1886).

[4] *Ibid.*, **104**, 976, 1430 (1887); **107**, 442 (1888). Ztschr. phys. Chem., **2**, 353 (1888). Ann. chim. phys., [6], **15**, 375 (1888).

solvents are the same when in their solutions the ratio of the number of molecules of solute to that of the solvent is the same.

Raoult indicated the possibility of employing the lowering of the vapor-pressure of a solution in determining the molecular weight of a dissolved substance. In his opinion, however, the experimental difficulties were such as to give preference to the cryoscopic and ebullioscopic methods.[1] Both Tammann[2] and Raoult[3] have called attention to the possible errors in measuring vapor-pressure which arise from the presence of dissolved gases and from variations in surface concentration due to unequal evaporation or condensation.

Numerous attempts have been made to devise a ready and accurate method for measuring the vapor-pressure of a solution.[4] Raoult[5] and the most of the experimenters before him employed the barometric vacuum over mercury. Beckmann[6] undertook the study of such measurements with the avowed purpose of designing an apparatus which could be used practically in determining the molecular weight from the lowering of the vapor-pressure.

He had recourse to the static method and employed first of all a modification of the barometric vacuum. The difficulties encountered, however, led him to abandon this. A partially static method gave somewhat better results, but it likewise proved inferior to the ebullioscopic method, to which he thereafter directed his attention.[7]

Dynamical methods of measuring the vapor-tension have also been worked out with varying degrees of success. The essential feature of one of these, first suggested by Ostwald, consists in determining the relative lowering of the vapor-pressure from the ratio of loss of weight of solvent to gain in weight of an absorption bulb, when a slow current of air is

[1] Ztschr. phys. Chem., **2**, 372, 373.

[2] Wied. Ann., **32**, 683 (1887).

[3] Ztschr. phys. Chem., **2**, 359.

[4] Moser: Wied. Ann., **14**, 72 (1881); Bremer: Rec. trav. chim. Pays-Bas., **6**, 122 (1887); and others.

[5] Ztschr. Chem., *loc. cit.*; Jour. de Phys., [2], **8**, 1 (1889).

[6] Ztschr. phys. Chem., **4**, 532 (1889).

[7] *Loc. cit.*

passed, in order, through solution, solvent, and absorption bulb.[1]

Kahlbaum[2] compares the static and dynamic methods and shows that both should yield like results.

Differential manometers of various forms for the direct measurement of differences in vapor-pressure have been suggested by Loeb,[3] Lord Kelvin,[4] Bleier and Kohn,[5] and others.

The following brief investigation was undertaken with the view of securing a serviceable apparatus for measuring, according to the static method, the difference in vapor-pressure between solution and solvent, and at the same time of simplifying the calculation of the molecular weight without introducing errors sufficiently large to vitiate the results.

As has been shown by Raoult, the lowering of the vapor-pressure of a solvent due to the presence of a non-volatile solute may be expressed by the well-known equation,

$$\frac{f-f'}{f} = \frac{n}{n+\mathrm{N}}.$$

When the concentration is low (not exceeding 7 molecules of solute to 100 molecules of solvent) there is equally applicable, as shown by the same investigator,[6] the expression

$$\frac{f-f'}{f} = \frac{n}{\mathrm{N}}.$$

Indeed this was the form first employed by Raoult in studying variations in vapor-tension.

In using the following apparatus there is no need that the molecular concentration should exceed that named. In these and similar determinations it is, consequently, much simpler to employ Raoult's second formula, $\frac{f-f'}{f} = \frac{n}{\mathrm{N}}$. We may regard as the "molecular depression" the diminution in vapor-tension of 100 grams of the solvent, produced by 1 gram

[1] Walker: Ztschr. phys. Chem., **2**, 602 (1888); Will and Bredig: Ber. d. chem. Ges., **22**, 1084 (1889); Orndorff and Carrell; J. phys. Chem., **1**, 753 (1897).

[2] Ztschr. phys. Chem., **6**, 594 (1890); **13**, 14 (1894).

[3] *Ibid.*, **2**, 606.

[4] Nature, **58**, 273, 295 (1897).

[5] Monatsh. Chem., **20**, 505, 909 (1899).

[6] Compt. rend., **104**, 976.

molecular weight of substance dissolved in it. If we represent this constant by K and the number of grams of substance and of solvent by P and W, respectively, we readily obtain for a given solvent at a given temperature the equation,

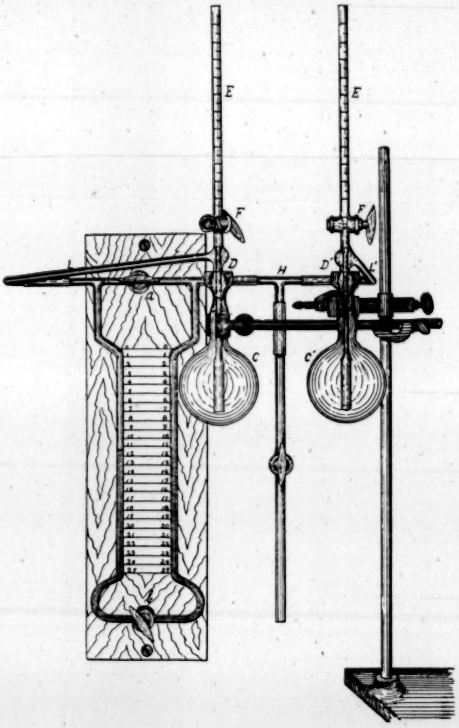
$$M = K\frac{100}{f-f'}\cdot\frac{P}{W}.$$

This expression, which, as we see, is identical with that for the boiling-point apparatus of Beckmann, renders it unnecessary to ascertain the direct vapor-pressure of either solution, or solvent.

The apparatus used is adapted to measure directly the lowering of the vapor-pressure, $f-f'$. A differential manometer with an inner diameter of 4 mm. is provided with two glass stop-cocks, *a* and *b*. The flasks, *C* and *C'*, into which, respectively, solution and solvent are introduced, are of nearly the same capacity (about 250 cc. each). The capillary tubes *L L'* connecting the flasks with the manometer are of equal length and form one piece with the ground-glass stoppers *D D'*.

The attachment between capillary tubes and manometer is made with heavy-walled rubber tubing. Tubes *E E'*, with glass stop-cocks at *F F'*, pass through the stoppers to within 1 to 2 cm. of the bottom of the flasks. The upper portions of these tubes are graduated to 0.1 cc. and should have a capacity of 10 to 15 cc. To insure against leakage, the ground-glass connections *D D'* are further sealed with mercury. A T at point *H* permits a ready exhaustion of the apparatus.

In conducting a determination, the flasks are held at a fixed temperature by immersion in a suitable thermostat. Stop-cock *a* is then opened, *b* closed, and the apparatus partially exhausted. Equilibrium is determined by the constancy of the manometric fluid when *b* is opened and *a* closed. Both stop-cocks of the manometer are now closed and into each flask, respectively, is introduced an equal volume of solution and solvent. After a few minutes *b* is opened and the reading taken when the height of the manometric fluid has become constant. Olive oil was used in the manometer, and this was



chosen chiefly because of its low vapor-tension. With a reduction of the internal pressure to about 300 mm. of mercury, equilibrium is usually attained in fifteen to twenty minutes.

In measuring vapor-pressures the increased concentration of the solution due to the partial evaporation of the solvent, will lead, as Raoult[1] has indicated, to erroneous results, if no

[1] Ztschr. phys. Chem., *loc. cit.*

correction be made for this error. In the above apparatus this source of error is rendered negligible in the calculation by the introduction of a sufficient quantity of the solution (10 to 15 cc.).

As already noted, inaccuracies arise in such determinations from surface concentration.[1] This difficulty is obviated in the present case by the large surface of the liquid and by slightly agitating the flask. There was further indicated the necessity of eliminating from solution and solvent, when measuring their vapor-pressure, all foreign volatile substances such as gases. As may be readily seen, this source of error is negligible in the apparatus considered, provided only that the gaseous content of solution and solvent is the same. With this end in view, both liquids are introduced under as nearly as possible the same conditions of temperature and pressure. The slight difference in air-solubility naturally subsisting between solution and solvent is here ignored.

In the change of position of the manometric liquid, the equilibrium of the air-content of the two flasks is slightly disturbed. This will invariably render the observed difference in vapor-pressure less than that actually existing. The error here introduced, however, is proportional to the observed difference and consequently disappears in the constant K when this latter is experimentally determined.

The slight contamination of the liquids introduced by vaseline or similar lubricant on the stop-cocks $F F'$, might be considered as a source of error, but the results obtained indicate that this may be disregarded.

The solvent used in any case should not have a vapor-pressure much less than 225 mm. of mercury. Consequently, in employing liquids of lower vapor-pressure, it is better to work at a correspondingly higher temperature.

It was found that invariably the most satisfactory results were obtained by taking the mean of two determinations, the solution and the solvent in the two cases being interchanged between the two flasks. Each of the following readings represents the mean of two such determinations.

[1] Tammann and Raoult: *Loc. cit.*

The ether and carbon bisulphide used were carefully purified, the former being distilled over sodium.

Temperature variations in the thermostat were held within 0°.15 C.

The pressure was reduced to 295–305 mm. and into each flask were introduced 10 cc. of liquid.

TABLE I.

Solvent, ether; K = 260.00; Temperature, 15°.

Naphthalene.

$\frac{P}{W}$	$f-f'$ in cm.	Molecular weight found	Molecular weight calculated.
0.0639	13.3	124.9	128
"	13.0	127.8	"
0.06565	13.3	128.4	"
"	13.33	128.0	"
0.0689	13.85	132.3	"
"	13.94	128.5	"
"	14.0	128.0	"

Cinnamic Acid.

0.05922	10.25	150.2	148
0.06716	11.65	149.9	"
"	12.0	145.5	"

Salicylic Acid.

0.06549	12.4	137.3	138
"	13.0	131.0	"
"	12.6	135.1	"

Iodine.

0.07139	7.4	250.8	254
"	7.5	247.5	"
"	7.3	254.2	"
"	7.4	250.8	"

Solvent, carbon bisulphide; K = 171.50: Temperature, 15°.

Naphthalene.

0.0851	11.0	132.7	128
"	11.2	130.3	"
0.07348	9.9	127.3	"
"	9.7	129.9	"

Phenanthrene.

$\frac{P}{W}$	$f-f'$ in cm.	Molecular weight found.	Molecular weight calculated.
0.06025	6.05	170.8	178
0.06971	7.05	169.6	"
"	7.00	170.8	"

Sulphur.

0.07435	4.9	260.2	256
"	"	"	"

Phosphorus.

0.07881	10.45	129.3	124
"	10.3	131.2	"

Iodine.

0.08115	5.5	253.0	254
"	5.8	240.0	"
"	5.4	257.8	"

The molecular weight of iodine as above determined is of some interest in view of the speculation that has obtained regarding the molecular aggregation of the element in different solvents. As is well known, iodine dissolves in some liquids as carbon bisulphide and the hydrocarbons with a violet color, in still others as alcohol, ether, and other alcoholic derivatives with a brownish-yellow color. Other solvents again yield intermediate gradations of color. It was early inferred that the color differences were due to a difference in molecular aggregation, and some of the experimental data seemed to favor this conclusion. Wiedemann[1] called attention to the fact that the solution in carbon bisulphide, when cooled with carbon dioxide and ether, became brownish-red. This result, doubted by Arctowsky,[2] was later confirmed by Krüss and Thiele.[3] On the other hand, brown solutions in the esters of the fatty acids become violet on warming to 80° C. Gautier and Charpy[4] for a time thought that they had discovered a difference in chemical behavior between violet and brown solutions.

[1] Wied. Ann., **269**, 580 (1888).
[2] Ztschr. anorg. Chem., **6**, 403 (1894).
[3] *Ibid.*, **7**, 70 (1894).
[4] Compt. rend., **111**, 645 (1890); Compare Beckmann and Stock: Ztschr. phys. Chem., **17**, 130 (1895).

The difference in the absorption spectra of variously colored solutions was also advanced as indicating a difference in molecular complexity.[1]

An attempt was made by Loeb,[2] working under Ostwald, to determine the molecular condition of iodine in solution from the change in vapor-pressure of the volatile solvent. His results led him to believe that in ether the molecule is I_4, while in carbon bisulphide it lies between I_2 and I_4. His method, however, was difficult to carry out, and ignored several of the sources of error already considered.

The careful work of Beckmann,[3] Nernst,[4] Krüss and Thiele,[5] and others,[6] has, however, shown conclusively that the molecule of iodine in the different solvents studied is diatomic, irrespective of the color of the solution.

Alcohol, as a solvent, does not readily lend itself to the determination of the molecular weight of iodine. Of the two methods commonly employed in such determinations, one is inapplicable because of the low freezing-point of the solvent, and the other appears to be somewhat unreliable because of the action of the element on boiling alcohol.[7] At the same time it may be noted that fairly concordant results have been obtained by the latter method.[8] The vapor-tension of alcohol at 15° to 20° is insufficient to afford trustworthy data by employing at those temperatures the apparatus described in this paper.

In connection with the results as tabulated above, an attempt was made to measure the osmotic pressure of a solution of iodine in alcohol.

The first exact quantitative measurements of osmotic pressure we owe to the painstaking work of Pfeffer.[9] He employed aqueous solutions and showed very clearly in such

[1] Compt. rend., **110**, 189; Rigollot: *Ibid.*, **112**, 38 (1891).
[2] Ztschr. phys. Chem., **2**, 606.
[3] *Ibid.*, **3**, 76 (1889); **17**, 107 (1895).
[4] *Ibid.*, **6**, 16 (1890).
[5] Ztschr. anorg. Chem., **7**, 52 (1894).
[6] Hertz: Ztschr. phys. Chem., **6**, 358 (1890).
[7] Krüss and Thiele: Ztschr. anorg. Chem., **7**, 61.
[8] Beckmann and Stock: Ztschr. phys. Chem., **17**, 117.
[9] Osmotische Untersuchungen, Leipzig, 1877.

cases the close relation between the osmotic pressure and the molecular concentration of the dissolved substance.

Since Pfeffer's work but little advance has been made in the methods of measuring osmotic pressure, although recently Morse and Frazer[1] have prepared a cell which seems to be particularly well adapted for recording high pressures. Aside from indirect determinations, however, such as those which may be derived from the boiling- or freezing-point methods or from the method suggested by Noyes and Abbott,[2] apparently no attempt has yet been made to measure directly the osmotic pressure of solutions other than aqueous.

In the following measurements a slight modification of Pfeffer's apparatus was used. It was found to be a comparatively simple matter to obtain serviceable cells in aqueous solutions, but the successful employment of these cells in alcoholic solutions proved somewhat difficult. The results obtained, however, point conclusively to the diatomic condition of iodine in the solvent and confirm the ebullioscopic determinations of Beckmann and Stock.[3]

A porous clay cell of about 25 cc. capacity was treated successively with dilute potassium hydroxide and hydrochloric acid (about 3 per cent), and was finally well washed with distilled water. Into the neck of the cell was then sealed securely with Portland cement a glass T. As soon as the cement had hardened, the cell was thoroughly injected with water and a membrane of copper ferrocyanide deposited according to the method employed by Pfeffer. A semi-permeable membrane was formed in this way, which would readily support a pressure of 1 atmosphere. The cell thus prepared was freed from soluble salts by prolonged treatment with distilled water. It was then transferred through water-alcohol of gradually increasing alcoholic strength to the ordinary 95 per cent alcohol.

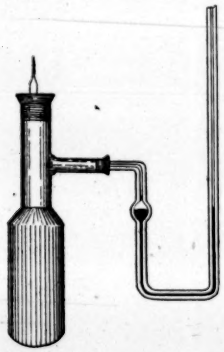
An open manometer, with a capillary tube of 1.5 mm. inner diameter, was used to record the pressure. Variation in the

[1] This JOURNAL, **26**, 80 (1901); **28**, 1 (1902).

[2] Ztschr. phys. Chem., **23**, 56 (1897); also Goodwin and Burgess: Phys. Rev., **7**, 171 (1898).

[3] *Loc. cit.*

concentration of the solution due to interaction of the iodine and the mercury of the manometer extended only a few centimeters along the capillary above the surface of the mercury. The cell was closed and connected with the manometer by



ordinary well-fitted corks, which were sealed externally to the glass ⊤ to preclude possibility of slipping.

The use of copper ferrocyanide as a membrane with iodine is not, as might be supposed, open to objection because of the oxidizing influence of the latter. While chlorine and bromine act upon this salt immediately, it is unaffected, at the ordinary temperature, after an hour's contact with an alcoholic solution of iodine such as was used in these determinations.[1]

The rise of the mercury in the manometer was much more rapid with alcoholic than it was with aqueous solutions of corresponding molecular concentration. The maximum pressure was attained in sixty to seventy-five minutes, and this pressure remained constant for nearly the same length of time. The molecular weight was calculated from the expression,

$$M = 22.4 \times 760 \times (1 + \alpha t)\frac{R}{P},$$

[1] That no change had occurred was shown by filtering and titrating the filtrate in the usual way with a solution of thiosulphate.

where M is the molecular weight, R the amount of substance dissolved in 1 liter of the solution, and P the osmotic pressure expressed in mm. of mercury.

TABLE II.

R.	Temperature.	P.	Molecular weight found.	Molecular weight calculated.
3.98	12°	265.1	266.8	254
4.14	17°	260.3	287.6	"
4.14	17°	277.8	269.5	"

In the above measurements of osmotic pressure I have been assisted by Miss Myra Winn, and in those of vapor-pressure by Mr. M. L. Chappell, and I take this occasion to express my appreciation of their earnest and careful work.

CHEMICAL LABORATORY, UNIV. OF CALIFORNIA, BERKELEY, CAL.,
December 20, 1902.

DIPHENYLSTYRYLCARBINOL.

BY ELMER P. KOHLER.

Results recently obtained by a number of investigators show that there is a remarkable difference between the properties of those tertiary alcohols which contain at least one alkyl group and those which contain only aryl groups. Substances like diphenylmethylcarbinol behave essentially like tertiary alcohols that contain only alkyl groups,[1] while triphenylcarbinol and its substitution-products are far more reactive than any aliphatic alcohols. They are easily reduced to the corresponding hydrocarbons,[2] they react, in the cold, with hydroxylamine and acid sulphites,[3] they can be condensed with substances like aniline and phenol,[4] and they combine with strong acids to form colored salts.[5] In view of these differences it was important to prepare and study tertiary alcohols which, like diphenylstyrylcarbinol,

$$(C_6H_5)_2(C_6H_5CH : CH)COH,$$

[1] Klages: Ber. d. chem. Ges., 35, 2646.
[2] Herzig and Wengraf: Monatsh., 22, 604.
[3] Baeyer and Villiger: Ber. d. chem. Ges., 35, 3016.
[4] Baeyer and Villiger: *Ibid.*, 35, 3018.
[5] Kehrmann: *Ibid.*, 34, 3815.

and the corresponding substance with two double linkages,

$$(C_6H_5)_2(C_6H_5CH : CHCH : CH)COH,$$

contain at least one alkylene group.

This paper contains the results obtained by a study of the former of these substances.

I. Preparation and Properties of Diphenylstyrylcarbinol.

Diphenylstyrylcarbinol can be made by the general reactions that Grignard[1] employed for making tertiary alcohols. In the beginning considerable difficulty was experienced because of the difference in the way in which saturated and unsaturated compounds react with organic magnesium compounds. The reactions that were expected to give a magnesium derivative of the alcohol are represented by the following equations:

I. $C_6H_5CH : CHCOC_6H_5 + C_6H_5MgBr =$

$$C_6H_5CH : CHC(C_6H_5)_2OMgBr;$$

II. $C_6H_5CH : CHCO.OC_2H_5 + 2C_6H_5MgBr =$

$$C_6H_5CH : CHC(C_6H_5)_2OMgBr + Mg(OC_2H_5)Br;$$

III. $C_6H_5CH : CHCOCl + 2C_6H_5MgBr =$

$$C_6H_5CH : CHC(C_6H_5)_2OMgBr + Mg(Cl)Br.$$

None of these reactions, however, gave the desired substance when the quantities used were those calculated from the above equations—each gave a substance of much greater molecular weight.

The magnesium compound obtained by the first reaction, for example, when decomposed with ice-water, gave a substance whose composition and molecular weight are represented by the formula $C_{34}H_{30}O_2$. Since this corresponds to the

[1] Compt. rend., **132**, 1182.

composition of a substance formed by the condensation of 1 molecule of diphenylstyrylcarbinol, $C_{21}H_{18}O$, and 1 molecule of benzylideneacetophenone, $C_{15}H_{12}O$, it seemed evident that the magnesium compound first formed in accordance with reaction I. subsequently combines with a molecule of the unchanged ketone. The concentration, the temperature, and the general method of procedure were changed in a variety of different ways without any material effect on the final result. It was observed, however, that the reacting liquid turned to a pale-yellow color when approximately one-half of the calculated amount of ketone had been added, and a very fair yield of the desired alcohol was obtained when the liquid was poured into ice-water immediately after the appearance of the yellow color.

To get the unsaturated alcohol, therefore, it is necessary to use 2 molecules of the magnesium compound to one of the unsaturated ketone. The best results were obtained when the ethereal solution of the ketone was added, drop by drop, at the top of an inverted condenser, which was connected with a flask in which the magnesium compound was kept boiling rapidly. As soon as all the ketone had been added the magnesium compound was poured into cold dilute sulphuric acid, the ethereal solution distilled in a water-bath, and the residue purified by recrystallization from alcohol.

Fifty-four grams of benzylideneacetophenone added to a solution obtained by dissolving 12 grams of magnesium in 80 grams of brombenzene and 750 grams of ether, gave 64 grams of diphenylstyrylcarbinol—about 90 per cent of the calculated amount.

The analyses gave the following results:

I. 0.1554 gram substance gave 0.5036 gram CO_2 and 0.0895 gram H_2O.

II. 0.1912 gram substance gave 0.6181 gram CO_2 and 0.1121 gram H_2O.

	Calculated for $C_{21}H_{18}O$.	Found. I.	II.
C	88.12	88.36	88.16
H	6.30	6.39	6.51

The molecular weight was determined in boiling acetone.

Table I.

K = 17.10.

Acetone. Grams.	Substance. Grams.	Rise in boiling-point.	Molecular weight.
7500	0.6190	0.055	256
"	1.2100	0.108	276
"	1.7350	0.158	273
	Calculated for $C_{21}H_{18}O$,		286

Diphenylstyrylcarbinol crystallizes well in colorless needles, which melt at 96°. It is very soluble in acetone, chloroform, benzene, and boiling alcohol; moderately soluble in cold alcohol and ether; very sparingly soluble in low-boiling ligroin. Under diminished pressure it distils without decomposition. When slowly heated under atmospheric pressure, most of it distils unchanged. The remainder undergoes far-reaching decomposition, the distillate containing stilbene and benzophenone while the residue is a gum from which no pure substances could be obtained.

Halochromism.—The alcohol dissolves in concentrated sulphuric acid and forms a lemon-yellow solution from which water reprecipitates the original substance. Since the only alcohols which are known to exhibit this property of "halochromism" are triphenylcarbinol and its substitution-products, it was important to prove beyond the possibility of mistake that the change in color is not due to a trace of some impurity like an unsaturated ketone. The alcohol was therefore repeatedly recrystallized from each of the different solvents above referred to. Since this did not change the result, it was transformed into the chloride with phosphorus pentachloride; the chloride, which crystallizes better even than the alcohol, was carefully purified by recrystallization from glacial acetic acid and then changed back into the alcohol with zinc dust and acetic acid. The resulting alcohol gave the same shade and intensity of color as the original product.

Towards strong acids, therefore, diphenylstyryl alcohol behaves differently from tertiary alcohols which contain an alkyl group. Its halochromism is very weak. A comparison

with triphenylcarbinol, made by the method of Baeyer and Villiger,[1] showed that the halochromism of the latter is about three hundred times as strong as that of the diphenylstyrylcarbinol.

Reduction.—The alcohol is reduced only with the greatest difficultly and no reducing agent that attacked the hydroxyl group was found. Sodium and sodium amalgam, acting on the alcoholic solution of the substance, slowly reduce it, giving an oil. This does not combine with bromine, but forms an alcoholate with metallic sodium. It is probably the saturated alcohol.

Zinc and glacial acetic acid give a well defined solid. Ten grams of zinc dust were added to 5 grams of the alcohol dissolved in 50 grams of glacial acetic acid. After boiling the mixture for five hours, compact, lustrous prisms began to separate on the walls of the flask. After boiling for twenty hours the acid was poured into water and the solid that separated purified by crystallization from alcohol. The product is moderately soluble in chloroform and benzene; slightly soluble in glacial acetic acid, alcohol, and acetone; insoluble in ligroin. It crystallizes in small plates that melt at 195°.

The analyses gave the following results:

I. 0.1497 gram substance gave 0.4085 gram CO_2 and 0.0917 gram H_2O.

II. 0.1991 gram substance gave 0.6393 gram CO_2 and 0.1202 gram H_2O.

	Calculated for $C_{21}H_{19}O$.	Found. I.	Found. II.
C	87.8	87.5	87.6
H	6.6	6.8	6.7

The molecular weight was determined in boiling acetone.

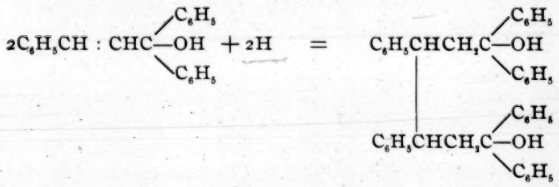
Table II.

K = 17.10.

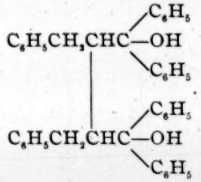
Acetone. Grams.	Substance. Grams.	Rise in boiling-point.	Molecular weight.
77.7010	0.2123	0.080	584
"	0.5338	0.200	589
	Calculated for $(C_{21}H_{19}O)_2$		574

[1] Ber. d. chem. Ges., 35, 3020.

The substance is evidently a dimolecular reduction-product formed according to the equation:



or



Oxidation.—Although diphenylstyrylcarbinol contains a double linkage it is not easily oxidized. Neither acid nor alkaline solutions of potassium permanganate attack it in the cold, and even boiling solutions of permanganate are reduced by it very slowly. Five grams of the alcohol were suspended in 750 cc. of a 5 per cent solution of sodium hydroxide. Potassium permanganate was added to the boiling liquid, in small quantities, until the color of the permanganate no longer disappeared. The liquid was then distilled in a current of steam which carried over an oil that solidified on standing. The resulting solid melted at 46° and gave a phenylhydrazone melting at 137°. It was pure benzophenone. The residue left after the distillation with steam was acidified, treated with hydrogen sodium sulphite to dissolve the oxides of manganese, and again distilled in a current of steam. The distillate contained only benzoic acid. The liquid left in the flask after the second distillation was extracted with ether, but no organic substance was found in it. The products of the oxidation were, therefore, benzoic acid and benzophenone.

The oxidation can be represented by the following equations:

$$\text{I. } C_6H_5CH:CHC(C_6H_5)_2OH + 4O = C_6H_5COOH + (C_6H_5)_2C(OH)COOH;$$

$$\text{II. } (C_6H_5)_2C(OH)COOH + O = (C_6H_5)_2CO + H_2O + CO_2.$$

A solution of chromic acid in glacial acetic acid slowly oxidizes the alcohol in the cold. Carbon dioxide is given off and the other products of oxidation are the same as those obtained with the boiling solution of alkaline permanganate.

Addition of Bromine.—The alcohol, dissolved in chloroform or carbon disulphide, slowly combines with bromine in the cold. The resulting addition-product is so unstable that it loses hydrobromic acid even when the solvent is evaporated in a vacuum. The only substance that was obtained in pure condition was a monobrom substitution-product. This is easily made by adding the calculated amount of bromine to a solution of the alcohol in chloroform, warming the mixture until the color of the bromine disappears, and pouring the product into boiling alcohol. On cooling the solution, pure bromdiphenylstyrylcarbinol crystallizes out in colorless plates that melt at 163°.

0.2740 gram substance gave 0.6922 gram CO_2 and 0.1158 gram H_2O.

	Calculated for $C_{21}H_{17}OBr$.	Found.
C	69.04	69.91
H	4.63	4.72

The substance is readily soluble in chloroform and ether, slightly soluble in alcohol.

Diphenylstyrylchlormethane.—Tertiary alcohols that contain an alkyl group readily react with hydrochloric acid and form the corresponding chlorides.[1] Triphenylcarbinol and its de-

[1] Klages: Ber. d. chem. Ges., 35, 2633.

rivatives react less readily with hydrochloric acid, but under suitable conditions these also are transformed into the corresponding chlorides.[1] Diphenylstyrylcarbinol does not seem to react with hydrochloric acid under any conditions. The dry gas was passed into the fused alcohol, into cold and boiling ethereal solutions of the alcohol, and into its solution in glacial acetic acid. In each case the substance was recovered unchanged. With phosphorus pentachloride, however, the hydroxyl group can be replaced by chlorine.

A mixture of 25 grams of the alcohol and 20 grams of phosphorus pentachloride was warmed on a water-bath. The reaction commenced at the melting-point of the chloride. As soon as hydrochloric acid ceased to be given off, the flask was connected with a pump and heated in a water-bath until all the chlorides of phosphorus were removed. The residue remained liquid when cooled in a freezing-mixture, but solidified almost immediately after it was poured into low-boiling ligroin. The resulting solid was purified by repeated recrystallization from low-boiling ligroin.

The analyses gave the following results:

I. 0.1896 gram substance gave 0.5737 gram CO_2 and 0.0969 gram H_2O.

II. 0.2282 gram substance gave 0.6900 gram CO_2 and 0.1150 gram H_2O.

	Calculated for $C_{21}H_{17}Cl$.	Found. I.	II.
C	82.73	82.61	82.50
H	5.58	5.63	5.58

The chloride crystallizes beautifully in large, lustrous, monoclinic prisms that melt at 91°. It is readily soluble in boiling alcohol and glacial acetic acid, moderately soluble in boiling ligroin and cold alcohol, almost insoluble in cold ligroin. The best crystals are obtained from glacial acetic acid.

Diphenylstyrylchlormethane is a remarkably inactive substance. After boiling it with a 10 per cent solution of sodium hydroxide for an hour, it was impossible to detect any chlorine in the solution. A boiling alcoholic solution of potassium hydroxide, however, slowly eliminates the chlorine and

[1] Baeyer and Villiger: *Ibid.*, **35**, 3031.

regenerates the alcohol. Zinc does not attack the substance when it is dissolved in indifferent solvents like benzene, alcohol, or ethyl acetate. In glacial acetic acid zinc dust slowly replaces the chlorine by hydroxyl. The process is greatly accelerated by the addition of a small quantity of copper acetate. The main product is always the carbinol. This is mixed with a small quantity of the dimolecular reduction-product previously described and a trace of an oil which appears to be an acetate, since it gives off acetic acid when distilled under diminished pressure.

II. Other Substances Obtained by the Reaction between Benzylideneacetophenone and Phenylmagnesium Bromide.

Under the preparation of diphenylstyrylcarbinol it was stated that when more than 0.5 molecule of benzylideneacetophenone is added to a solution of 1 molecule of phenylmagnesium bromide, the solution turns yellow. On further addition of ketone to this yellow solution a pasty mass separates from the solution. This increases in amount until 2 molecules of ketone have been added to 1 molecule of the bromide. When this paste is decomposed with water it gives a substance which, after recrystallization from acetone, melts at 180°.

An analysis of this substance gave the following results:

I. 0.2086 gram substance gave 0.6679 gram CO_2 and 0.1143 gram H_2O.

II. 0.1840 gram substance gave 0.5872 gram CO_2 and 0.1023 gram H_2O.

	Calculated for $C_{18}H_{18}O$.	Found. I.	II.
C	87.44	87.32	87.01
H	6.07	6.08	6.17

The molecular weight was determined in boiling acetone.

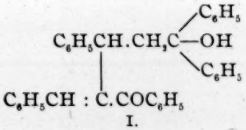
Table III.

K = 17.10.

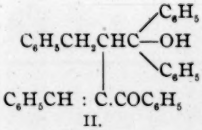
Acetone. Grams.	Substance. Grams.	Rise in boiling-point.	Molecular weight.
76.625	0.6023	0.027	498
"	1.1460	0.050	511
"	1.7970	0.080	500
	Calculated for $(C_{18}H_{18}O)_3$,		494

The substance is readily soluble in acetone, benzene, and boiling glacial acetic acid; sparingly soluble in alcohol and ether; insoluble in low-boiling ligroin. When distilled under a pressure of 20 mm. it decomposes into benzylideneacetophenone, diphenylstyrylcarbinol, and a yellow oil of unknown composition. It dissolves in concentrated sulphuric acid, forming a blood-red solution.

The structure of this substance has not yet been established with certainty, but the method of formation, composition, and behavior on distillation leaves no doubt that it results from the combination of 1 molecule of benzylideneacetophenone with 1 molecule of diphenylstyrylcarbinol. Since it dissolves in sulphuric acid and gives a deep-red solution, the union of the two substances probably takes place at the double linkage of the unsaturated carbinol, leaving intact the double linkage of the ketone. This leads to the possible formulas:



I.



II.

Each of these formulas explains the known properties of the substance. Formula I. is the more probable of the two since it represents a form of condensation that is known to take place with unsaturated acids[1] and unsaturated ketones.[2] In any case, since other unsaturated ketones give similar condensation-products, it will probably not be difficult to select materials in such a way that the structure of the product and, therefore, the general method of condensation can be determined by direct experiment.

The ethereal solution from which the magnesium derivative of the substance just described separates in the form of a paste, contains a third product of the reaction between benzylideneacetophenone and phenylmagnesium bromide. This is a

[1] Michael: J. prakt. Chem., [2], **35**, 349; **37**, 522. Auwers: Ber. d. chem. Ges., **24**, 307.

[2] Knoevenagel: Ann. Chem. (Liebig), **281**, 24. Kostanecki: Ber. d. chem. Ges., **29**, 1488.

magnesium compound which is soluble in ether and which is formed in much larger amount when 1 molecule of the ketone is added to 1 molecule of the bromide. On decomposition with water it yields a viscous liquid, which it has not yet been possible to get in a perfectly pure condition. The crude product contains a small quantity of diphenylstyrylcarbinol, which can be removed by oxidation with chromic acid, and some of the condensation product which can be removed by extracting the ligroin solution with small quantities of concentrated sulphuric acid. The residue left after removing the ligroin is a clear, colorless oil, which decomposes on distillation under diminished pressure. The distillate contains large quantities of stilbene mixed with a small quantity of benzophenone. The oil imparts a faint yellow color to sulphuric acid. It may be a tertiary alcohol formed by the action of phenylmagnesium bromide on the condensation-product described above.

The reaction between benzylideneacetophenone and phenylmagnesium bromide seems to take place in the following stages:

1. Every drop of the solution of the ketone produces a faint-yellow precipitate, which immediately redissolves as long as the solution contains at least 2 molecules of the bromide for every molecule of ketone. This is probably represented by the following equations:

I. $C_6H_5CH : CHCOC_6H_5 + C_6H_5MgBr =$

$$C_6H_5CH : CHC(C_6H_5)_2OMgBr ;$$

(Yellow precipitate.)

II. $C_6H_5CH : CHC(C_6H_5)_2OMgBr + C_6H_5MgBr =$

$$\left(C_6H_5CH : CHC(C_6H_5)_2OMgBr \right)(C_6H_5MgBr).$$

(Soluble in ether).

That such double compounds are capable of existing was shown by Grignard,[1] who found that allyl iodide forms the compound $C_3H_5I.C_3H_5MgI$, and that this compound does not give clean reactions.

If the mixture is decomposed with ice-water at this stage, the product is pure diphenylstyrylcarbinol.

2. The double compound reacts with more of the ketone:

$$\left(C_6H_5CH:CHC(C_6H_5)_2OMgBr\right)(C_6H_5MgBr) + 3C_6H_5COCH:CHCOC_6H_5 = 2\left(\begin{matrix} C_6H_5CH.CH_2C(C_6H_5)_2OMgBr \\ | \\ C_6H_5CH:CCOC_6H_5 \end{matrix}\right).$$

If the mixture is decomposed at this stage the product is the substance $C_{36}H_{30}O_2$.

III.
$$\begin{matrix} C_6H_5CH.CH_2C(C_6H_5)_2OMgBr \\ | \\ C_6H_5CH.CCOC_6H_5 \end{matrix} + C_6H_5MgBr =$$

$$\begin{matrix} C_6H_5CH.CH_2C(C_6H_5)_2OMgBr \\ | \\ C_6H_5CH:CC(C_6H_5)_2OMgBr \end{matrix}$$

The oil described above is probably the product of decomposition at this stage.

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[1] Ann. chim. phys., [7], **24**, 433.

THE ACTION OF ZINC ON TRIPHENYLCHLORMETHANE.

By M. Gomberg.

The recent paper by J. F. Norris and L. R. Culver,[1] under the above title, requires some corrections in regard to the references made by the authors to my papers.

Action of Sodium.

Norris and Culver[2] say: "It was shown in the same paper that, under certain conditions, triphenylchlormethane reacts with sodium, contrary to the observations of Gomberg." In turning to the first paper of Norris and Sanders, to which the reference is made, we find the following statement:[3] "The solution of the halogen compound (triphenylchlormethane) was allowed to stand two weeks in contact with sodium and, finally, was heated to boiling for an hour. As no change was apparent, the ethereal solution was decanted and evaporated to crystallization. The compound obtained was shown to be triphenylchlormethane." It was only on the addition of brombenzene to the above mixture that a reaction took place. In my short paper of two years ago the following explanation is given in regard to this reaction:[4] "Furthermore if the substance is really identical with the peroxide mentioned, it is not the result of the action of sodium upon a mixture of the two halogen compounds, but is formed by action of the atmospheric oxygen upon the unsaturated hydrocarbon (triphenylmethyl) which must have resulted in some way from the action of sodium upon triphenylchlormethane alone. Experiments show that small quantities of the triphenylmethyl are produced in this way."

Is the Reaction Quantitative?

Norris and Culver say:[5] "At the beginning of the work

[1] This Journal, **29**, 129 (1903).
[2] *Ibid.*, **29**, 130 (1903).
[3] *Ibid.*, **25**, 58 (1901).
[4] J. Am. Chem. Soc., **23**, 110 (1901).
[5] This Journal, **29**, 132 (1903).

it was found that the statement of Gomberg was incorrect, that when the reaction between zinc and triphenylchlormethane took place in benzene solution the metal reacts quantitatively according to the following equation:

$$2(C_6H_5)_3C.Cl + Zn = 2(C_6H_5)_3C- + ZnCl_2.''$$

In turning to the reference made by the authors to my paper in respect to this question, we see at once that there is no such statement either made or implied. We read:[1] "The zinc removes the halogen from triphenylchlormethane quantitatively." And this statement is based not upon the results of a "single," but of three experiments. That the whole of the chlorine is in the sirupy mass which separates in this reaction there was no doubt. But that the reaction, in so far as the production of triphenylmethyl is concerned, was not quantitative, I was well aware, and hence the statement on the very next page of the same paper:[2] "Twenty grams of the halogen compound (triphenylchlormethane) give about 12 grams of the peroxide." The theoretical quantity is 18.6 grams. In another paper, which appeared a few months later,[3] we find the following statement: "It was stated in my preliminary paper that only about two-thirds of the theoretical quantity of the unsaturated hydrocarbon is formed. The nature of the other products is being studied and I find that this varies according to the metal and solvent employed." Again, in a paper of still later date I say:[4] "Strictly quantitative experiments on samples of 20 grams of triphenylchlormethane proved that the hydrocarbon can be obtained in yields of from 85 to 90 per cent of the calculated amount." I have spent a great deal of time and labor in order to determine how nearly quantitative the reaction is. Many data have been accumulated, but their publication is deferred to a later date, because I believe conditions will be found which will give still better results. Such ideal conditions, it is thought, have been found in the action of molecular silver. The reaction has been al-

[1] J. Am. Chem. Soc., **22**, 761 (1900).
[2] *Ibid.*, **22**, 762 (1900).
[3] *Ibid.*, **23**, 110 (1901).
[4] *Ibid.*, **24**, 628 (1902). Compare especially J. Am. Chem. Soc., **24**, 600.

lowed to proceed for several months, but the products have not as yet been further examined.

Formation of the Double Salt with Zinc Chloride.

Norris and Culver say :[1] "During the course of the reaction a thick, dark mass separates, which Gomberg assumed to be a compound of benzene and zinc chloride. Gomberg, in a later paper, briefly mentioned this mistake, but he has reported no further work to test this point." The authors also describe how they found out that this gummy mass is a compound of zinc chloride and triphenylchlormethane. No analysis of this compound was made by the authors.

The following is a quotation from my third paper,[2] where the action of zinc upon triphenylchlormethane in ether is described : "The viscous mass which is formed at the beginning of the reaction is not zinc chloride, but a double salt of it with triphenylchlormethane. Zinc chloride, I find, is soluble in ether, while the double salt is not. The thick yellow mass which was described under the experiments with benzene is also a double salt of a similar or of identical composition, and not a compound of zinc chloride with benzene, as has been previously supposed. Such a double salt, when treated with water, would give up all its chlorine to the latter, and this accounts for the somewhat misleading results which were obtained in the estimation of chlorine in the insoluble residue from benzene. The same double salt is formed with the greatest readiness when a solution of zinc chloride in ether or in acetic ether is added to a solution of triphenylchlormethane in benzene or in absolute ether. All attempts to bring it to crystallization have failed, but a number of other double salts of triphenylhalogenmethanes, and especially of tritolylchlormethane, were obtained in sufficient purity to establish the remarkable tendency of these halogen bodies towards the formation of double compounds with metallic salts."

A more detailed description of the composition and of the reactions of these interesting compounds is to be found in my fourth paper.[3] Quantitative results, showing that the reac-

[1] This JOURNAL, **29**, 132 (1903).
[2] J. Am. Chem. Soc., **23**, 497 (1901).
[3] *Ibid.*, **24**, 601, 622 (1902).

tion in benzene proceeds probably according to the equation

$$3(C_6H_5)_3C.Cl + Zn = 2(C_6H_5)_3C + ZnCl_2.(C_6H_5)_3C.Cl,$$

are given in my sixth paper.[1]

Action of Zinc in Ethyl Acetate.

Norris and Culver then describe the action of zinc upon triphenylchlormethane in ethyl acetate. Their results confirm fully those given by myself: No hydrogen is given off; the unsaturated hydrocarbon is formed, which on exposure to air gives the peroxide. They also say:[2] "The filtrate from the peroxide, which contains about one-fourth of the organic reaction-product, has not received in the past the attention that it deserves. As triphenylmethane, triphenylcarbinol, and an oil are at times present, an investigation of the cause of the formation of these substances must be made before the reaction, which is evidently a very complex one, can be exactly interpreted." A detailed account of the methods employed by the authors in detecting and separating the above-mentioned products is then given. In my second paper, describing the action of zinc on triphenylchlormethane in acetic ester and the subsequent oxidation of the solution on exposure to air, the following statement is made:[3] "I have been at work for some time trying to determine what becomes of the remaining 20 per cent of the triphenylmethyl. I find some triphenylmethane, triphenylcarbinol, and a portion which cannot be brought to crystallization. It remains, however, to determine whether all these products are formed before or during the oxidation of the unsaturated hydrocarbon." The authors make no reference to these results.

Norris and Culver then describe a series of experiments, from which they draw the following conclusions: "The most evident facts are: First, that much more zinc is used than is called for by Gomberg's equation; second, that much more oxygen is absorbed than is contained in the peroxide; and third, that the percentage of peroxide obtained is less than that found by Gomberg."[4]

[1] Ber. d. chem. Ges., **35**, 3919 (1902).
[2] This JOURNAL, **29**, 132 (1903).
[3] *Ibid.*, **23**, 330 (1901).
[4] *Ibid.*, **29**, 137 (1903).

In regard to the first point, it may be said that the method of procedure employed by the authors in their experiments is such as to invalidate the conclusions drawn by them. They say that they found zinc hydroxide as one of the products of the reaction. Of course, the hydroxide could not have been formed in the reaction of zinc upon triphenylchlormethane. It might have come either from the oxidation of some zinc derivative formed in the reaction, or it might have been formed by the direct oxidation of the metal by the oxygen, under the influence of the different products present. If the latter is the case, it is evident that the quantity of zinc entering into the reaction, as found by Norris and Culver, represents really the sum of the quantities entering into two or more reactions. Furthermore, my own experiments, so far as they have gone, show a decidedly simpler relation. Some of the experiments have already been reported,[1] and others are still in progress.[2]

Absorption of Oxygen.

The authors find that much more oxygen is absorbed than is contained in the peroxide. Here again, the conclusion is invalidated because of the formation of zinc oxide. To be of value, the study of the oxidation process should be so conducted as to involve the oxidation of one substance only at a time. My own experiments in this direction were therefore made on pure triphenylmethyl, and it was shown that the unsaturated hydrocarbon takes up about 15 per cent more oxygen than would be required for the formation of the peroxide. Moreover, I also showed what becomes of at least a portion of this excess of oxygen: "Die Menge des aufgenommenen Sauerstoffs ist demnach grösser als die für die Bildung des Peroxyds erforderliche. Neben dem krystallinischen Peroxyd bildet sich auch ein gelbes Oel, welches .... 8.83 per cent Sauerstoff enthielt. Es ist ja auch möglich, dass der Verlauf des Oxydationsprocesses von der Natur des gebrauchten Lösungs-

[1] Ber. d. chem. Ges., **35**, 3919 (1902).

[2] There is good reason to think that a solution of zinc chloride in acetic ester dissolves metallic zinc. A strip of pure zinc lost in a 10 per cent solution of freshly fused zinc chloride in water only 0.0018 gram in two weeks. In a 10 per cent solution of the same zinc chloride in absolutely pure acetic ester the loss was 0.020 gram in twenty-four hours, 0.035 gram in five days, and 0.066 gram in two weeks. The ester itself had no effect upon the zinc. This product will be studied further.

mittel abhängig ist.''[1] No reference is made by Norris and Culver to the above-mentioned results. They were published almost a year and a half ago.

The Yield of the Peroxide.

That the equation,

$$2(C_6H_5)_3C.Cl + Zn = 2(C_6H_5)_3C + ZnCl_2,$$

represents the truth in so far as the formation of triphenylmethyl is concerned, is, I believe, true. But no claim has ever been made that this is, under all circumstances, the only reaction taking place. As has already been mentioned, I am still looking for such ideal conditions as would insure yields higher than 90 per cent of the theoretical. The yields obtained by me when the solvent employed was acetic ether, were from 75 to 78.5 per cent of the calculated quantity. Norris and Culver got, at least in one instance, 70 per cent,—not so very far from the yield obtained by myself.[2] The question naturally arises, why did they not get at least a similar yield in the other eight experiments? It may be true that "very slight changes in the conditions of the experiment have a marked influence on the result."[3] But when it is intended to draw conclusions from a quantitative study of a reaction, the first requisite is to learn to so control the conditions of the experiment as to insure approximately the same yield of the principal product under similar conditions. Otherwise, the results indicate merely that there is something wrong with the method of procedure. The yields of the peroxide as obtained by Norris and Culver vary from 29 to 70 per cent.[4] The question arises, what precautions were taken to insure that the reaction was carried to the end? What precautions were taken to prevent the zinc from becoming coated with a layer of the insol-

[1] Ber. d. chem. Ges., **34**, 2732 (1901).

[2] The experiments in regard to the yield of the peroxide were repeated again. 2.19 grams triphenylchlormethane gave 1.603 grams peroxide, which is equal to 78.8 per cent of the theory; 2.235 grams gave in another instance 1.575 grams peroxide, *i. e.*, 75.8 per cent of the theory. But as I have already shown, (Ber. d. chem. Ges., **34**, 2732), pure crystalline triphenylmethyl gives on oxidation only 86.5 per cent of the peroxide; the above percentages indicate the formation of 90.8 and 87 per cent of triphenylmethyl.

[3] This JOURNAL, **29**, 137 (1903).

[4] *Ibid.*, **29**, 137 (1903).

uble triphenylmethylperoxide? Such a layer would prevent the zinc from further action upon the triphenylchlormethane. The authors state that a small yield of the peroxide is always accompanied by a large yield of triphenylcarbinol. There may be, as the authors claim, a certain relation between these two products.[1] Still, as the authors did not assure themselves that the action of zinc on triphenylchlormethane was carried to the end, *i. e.*, that all of the halogen compound was attacked by the metal, and as they treated the reaction-products with water, it is evident that any unchanged triphenylchlormethane would be converted by this treatment into the triphenylcarbinol.

Conclusion.

The claim of Norris and Culver that "the work already done brought to light a number of facts overlooked by Gomberg," cannot, as has been shown, be upheld. The yield of triphenylmethyl, which was somewhat smaller than the calculated, the formation of the double salt of zinc chloride with triphenylchlormethane, the formation of some triphenylmethane, carbinol, and of an oil, when acetic ether is the solvent in the reaction of zinc upon triphenylchlormethane, the absorption of somewhat more than the calculated quantity of oxygen even by the pure triphenylmethyl—these facts have all been discussed in my papers, if not in the first, then in some of the later ones.

In conclusion, the authors say that "where so many reactions are taking place simultaneously there is a chance that there may be subtle changes going on which the experimental data, so far collected, do not lead us to suspect."[2] This, indeed, is a truism and requires no further argument. New facts may be discovered at any time which will make it advisable to assign to the unsaturated hydrocarbon a constitution other than that involving the hypothesis of a trivalent carbon atom —a hypothesis which so far has proved very useful in explaining old facts and suggesting new ones. But from what has

[1] I have already shown (Ber. d. chem. Ges., 33, 3916) that triphenylmethyl can be oxidized to triphenylcarbinol.

[2] This JOURNAL, 29, 140.

been given in this paper it is evident that the complexity of the reaction, which Norris and Culver attribute to the action of zinc upon triphenylchlormethane, represents in reality the sum of several reactions: (1) The action of the metal upon the halogen compound; (2) the oxidation of the metal and of the unsaturated hydrocarbon in the presence of several other products; (3) the action of zinc oxide so formed upon some still unchanged triphenylchlormethane;[1] and (4) treatment of the reaction-products with water. It has been my aim, in studying quantitatively the action of metals upon triphenylchlormethane, to separate these reactions from each other as much as possible. It was announced in my fourth paper[2] that this phase of the problem is being thoroughly studied and that the results will be published in a later paper.

The acknowledgment by Norris that the experimental evidence put forward by him in the paper of two years ago[3] was, as I showed,[4] faulty, removes from the literature the only experimental evidence that has so far been suggested against the constitution of the unsaturated hydrocarbon as triphenylmethyl.

And as for the "new" facts presented by Norris and Culver, I fully agree with the authors "that none of the facts can be used as evidence against the existence of triphenylmethyl."

ANN ARBOR, MICH., Feb. 14, 1903.

Contributions from the New York Agricultural Experiment Station.

III.—A CONTRIBUTION TO THE CHEMISTRY OF AMERICAN CHEDDAR CHEESE.

BY LUCIUS L. VAN SLYKE AND EDWIN B. HART.

INTRODUCTION.

As cheese ages or ripens, the nitrogen compounds present in the fresh cheese undergo changes in composition more or less profound in character. To the general process that embraces these and other changes is applied the term "cheese

[1] I have prepared triphenylmethyl oxide, $(C_6H_5)_3C—O—C(C_6H_5)_3$, from triphenylchlormethane and silver oxide. It will be described in detail later.

[2] J. Am. Chem. Soc., **24**, 628 (1902).

[3] This JOURNAL, **25**, 117 (1901).

[4] *Ibid.*, **25**, 317 (1901).

ripening." In a thorough study of the cheese-ripening process, it is of fundamental importance that we ascertain what specific compounds are formed. We must possess such knowledge before we can understand fully in what way different conditions affect the ripening process. The more complete our knowledge is in respect to the various individual compounds formed in cheese-ripening, the better can we understand the causes that produce, and the conditions that control, the process. Whether or not cheese-ripening is in part, or in whole, a biological process, our knowledge of the details of the process must depend very largely upon our knowledge of the specific chemical compounds resulting from such action.

More or less work of a desultory character has been done in this field. Special difficulties are met in the isolation and study of the individual proteolytic compounds found in cheese, owing to a lack of knowledge regarding the chemical constitution of many of them and also to the minute quantities commonly available. Then, too, the same compounds are present or absent according to the conditions of ripening, even in cheese of the same variety. In different kinds of cheese there is still greater variation. Thus far, we have confined our attention to the study of American cheddar cheese, the type most commonly made in this country.

The presence of ammonia was early noticed in cheese. In 1818 Proust[1] discovered in old cheese leucine, which he called "caseous oxide." In 1880 Sieber[2] found tyrosine in a sample of Roquefort cheese. In 1882 Weidmann[3] undertook an investigation of the chemical compounds of Emmenthaler cheese more thorough than had been previously attempted. He was the first to call attention to a product soluble in hot alcohol, called by him "caseo-glutin," which we have recently shown to be unsaturated paracasein lactate.[4] Rose and Schulze,[5] in 1885, were the first to mention the presence of

[1] Ann. chim. phys., [2], **10**, 40 (1818).
[2] J. prakt. Chem., N. F., **21**, 213 (1880).
[3] Landw. Jahrb., **11**, 587 (1882).
[4] This JOURNAL, **28**, p. 429, (1902).
[5] Landw. Versuchst., **31**, 115 (1885).

nuclein in cheese, though their work was largely qualitative. In 1887 Benecke and Schulze[1] added to the list of nitrogen compounds, previously found in Emmenthaler cheese, phenylamidopropionic acid. Recently Winterstein and Thöny[2] have reported in Emmenthaler cheese the following compounds: Histidine, lysine, guanidine probably, tetramethylenediamine (putrescine), and pentamethylenediamine (cadaverine). In very few cases do we know anything of the history of the cheese used in the investigations. In our work we are familiar in most cases with the history of the cheese, including the conditions of manufacture and of ripening.

EXPERIMENTAL PART.

Paranuclein (*Pseudonuclein*).

In the work first done, about ten years ago, in this laboratory in the study of cheese-ripening, a substance was precipitated by dilute acids from the water-extract of cheese, showing the general chemical behavior of milk-casein toward different reagents. This was called "soluble casein" in the absence of knowledge of its specific chemical composition. During the past three years we have given more or less attention to the study of this substance and, though our work is still incomplete, we present here the results obtained up to the present time.

The fact that the substance in question was precipitated by dilute acids, completely by 0.2 per cent hydrochloric acid, suggested its resemblance to Chittenden's so-called casein-dyspeptone,[3] the insoluble substance obtained in larger or smaller quantities when milk-casein is digested with pepsin and hydrochloric acid.

The substance is obtained from cheese by extraction with water and precipitation by hydrochloric acid. We cover about 3 kilograms of finely ground cheese with water, digest it at 55° C. for half an hour, and then decant the extract. The residue is again covered with water, digested, and decanted as before, this operation being repeated several times until the

[1] Landw. Jahrb., 1887, 317.
[2] Ztschr. physiol. Chem., **36**, 28 (1902).
[3] "Studies in Physiol. Chem.," Yale Univ., **3**, 66 (1887-8).

extract amounts to 4 or 5 liters. After filtration through absorbent cotton the solution is cooled to 10° C., or lower, and allowed to stand until the fat separates on the surface as a solid layer, which can be readily removed. The solution is then heated to 50° to 55° C. and treated with enough hydrochloric acid to equal 0.2 per cent of the solution. The paranuclein separates as a flocculent, white precipitate, settling to the bottom of the vessel, leaving a supernatant liquid of a bright-yellow color. The separation of the precipitate may be hastened by vigorous stirring. The precipitate is filtered, washed with water, and then dissolved in 1 or 2 liters of 1 per cent solution of sodium carbonate. The resulting solution appears to be complete, though it is milky in appearance. It is filtered, reprecipitated by dilute hydrochloric acid, and the precipitate is filtered and washed. This process of redissolving and reprecipitating is repeated three or four times in all. From this point, two different methods may be employed for further purification of the substance. By one method, the third or fourth precipitate by hydrochloric acid is thoroughly washed with water containing dilute hydrochloric acid, then with alcohol, and finally with ether, after which it is extracted by boiling ether for several days, until all traces of fat are removed. It is then dried to constant weight at 105° to 110° C. for analysis. By the other method, the third or fourth solution in dilute sodium carbonate is made exactly neutral by hydrochloric acid, treated with 3 per cent of chloroform to prevent any bacterial action, and dialyzed in running water until all chloride is removed. The resulting solution is concentrated on the water-bath to a thick syrup, and while still warm is poured into a mixture of 95 per cent and absolute alcohol. This is allowed to stand two or three days. A white, gelatinous coagulum results, which is filtered, washed thoroughly with alcohol, placed under absolute alcohol several days, again filtered, treated with cold ether, then dried, powdered, and extracted with boiling ether until all fat is removed. It is then finally dried to constant weight at 105° to 110° C. This method of dialyzing, concentrating, and then precipitating by alcohol in neutral or alkaline solution appears usually

to carry down with the precipitate large quantities of ash. Jackson[1] has pointed out this fact and has shown that this may be avoided by using the first method given above or by precipitating with alcohol in the presence of dilute acid.

We present in the table below the results of analyses of samples of the substance prepared from different cheeses. The figures given are on the basis of ash-free substance. The first five samples were prepared by dialysis and precipitation by alcohol in neutral or slightly alkaline solution, except sample 3, in which case the solution was probably slightly acid. The other samples were prepared by the first method described above. In samples 6, 7, and 8 the amount of material obtained was not sufficient for making all the determinations.

An examination of the results indicates that we probably did not succeed in freeing the substance from impurities. The few analyses of nuclein on record show considerable divergence. In comparison with Chittenden's casein-dyspeptone, the content of nitrogen, hydrogen, and carbon is lower in our substance, while the sulphur is considerably higher. Chittenden regarded the phosphorus as consisting entirely of calcium phosphate, but Jackson[1] has shown that paranuclein yields over 2 per cent of organic phosphorus, if care is taken to prevent calcium phosphate from being precipitated with the substance and to avoid the formation of inorganic phosphates during ignition. We shall give our attention further to methods of separating paranuclein from cheese in the hope of being able to prepare it free from impurities and studying its decomposition-products.

Paranuclein results from the breaking down of casein or paracasein and is always found in the water-extracts of ripening cheese. The amounts commonly found in cheese under different conditions we shall discuss in a future paper.

Amido Compounds.

In the work, an account of which follows, we planned to isolate such diamido compounds as might be present in the cheese examined. Two different cheeses of the normal Ameri-

[1] Am. J. Physiol., 4, 170 (1900).

Table I.—Analyses of Preparations of Paranuclein Obtained from Different Cheeses.

	C.	H.	N.	S.	P.	O.	Ash.
1. Cheese bought in open market, three months old	48.51	6.81	14.14	3.19	2.50	24.95	31.53
2. " " " " " " " "	48.46	5.67	13.25	2.00	2.23	28.39	23.65
3. " four and a half months old	52.01	6.98	14.17	1.65	1.41	23.78	1.44
4. " seven months old, interior	50.60	7.00	13.65	1.00	1.33	26.32	16.64
5. " " " " exterior	50.56	7.70	14.36	0.86	1.52	25.00	20.22
6. " one month old	46.72	6.86	15.91	....	....	....	....
7. " two months old	47.59	6.90	12.36	....	....	....	....
8. " three " "	48.82	7.43	12.98	....	....	....	....
9. " four " "	50.56	6.73	12.96	0.83	1.13	27.79	3.10
10. " five " "	53.12	6.51	13.68	0.89	0.98	24.82	4.42

can cheddar type were used to furnish material for our work. One was four and a half months old, had been ripened at a temperature of 18° C., and possessed a mild and pleasant flavor. The other was fifteen months old, had been ripened at a temperature of about 20° C., and possessed a somewhat pungent but not disagreeable flavor. In preparing the samples for examination, the cheese was cut into small pieces, the rind being excluded. We used 8 to 10 kilograms of each cheese. After drying in air at room temperature, the cheese was placed in large bottles, covered with 95 per cent alcohol, and digested for several days at room temperature, with frequent agitation. The resulting alcoholic solution, which was of a rich yellow color, was filtered through filter-paper from the insoluble portion, the latter being allowed to drain thoroughly. The insoluble residue was then dried at 60° C., in order to remove all alcohol, and furnished a white, crumbly mass. Most of the fat had been removed by the alcohol, and probably some small proportion of the amido-acid compounds. This white mass was next extracted with several portions of water at 55° C., and the extracts filtered through absorbent cotton until about 25 liters of extract were obtained. This water-extract was treated with tannin in excess, a copious precipitate of caseoses and peptones resulting, which was removed by filtration. The excess of tannin in the filtrate was removed by careful addition of lead acetate, until a drop of the reagent gave no further turbidity, after which the precipitate of lead tannate was filtered and washed with water. The excess of lead in this filtrate was then carefully removed by the addition of sulphuric acid, until a drop gave no additional precipitate, the final traces of lead being removed by hydrogen sulphide. The filtrate from the precipitates of lead sulphate and lead sulphide were united, concentrated to small volume on a water-bath, then made alkaline with barium carbonate, and finally boiled about fifteen minutes in order to remove all ammonia. The solution was then made slightly acid with sulphuric acid, the precipitated barium sulphate removed by filtration, and the filtrate made to contain 5 per cent acid by adding sulphuric acid, after which it was precipitated by

phosphotungstic acid. A heavy crystalline precipitate resulted, which was filtered and washed with 200 cc. of 5 per cent sulphuric acid. The phosphotungstic acid precipitate was then suspended in water and treated with barium hydroxide to remove the phosphotungstic acid in the well-known way. The excess of barium was removed by carbon dioxide, the precipitate filtered and washed. This gave a solution which should contain the hexon bases, *viz.*, arginine, lysine, histidine, and lysatine. For the separation of the first three compounds, the Kossel-Kutscher method was employed, and for lysatine, Siegfried's method. To this solution, diluted to 2 liters and made slightly acid by sulphuric acid, was added a solution of silver nitrate, until a drop of the solution, placed on a white porcelain surface, gave with barium hydroxide the yellow precipitate of silver oxide, thus showing excess of silver nitrate. Then barium hydroxide was added to saturation, which formed a somewhat slimy precipitate, filtering slowly. The precipitate was filtered and washed with a saturated solution of barium hydroxide. The filtrate (Solution A) was worked for lysine, and the precipitate for lysatine, histidine, and arginine. The precipitate was suspended in warm water and the barium carefully removed by means of sulphuric acid and the silver by hydrogen sulphide. The precipitate was filtered, washed with water, and the filtrate made to 1 liter (Solution B).

In Cheese Fifteen Months Old.—In 10 cc. of Solution B the nitrogen was determined and found to be 0.00041 gram, or a total of 0.041 gram in the entire extract. This small amount of nitrogen indicates that arginine, histidine, and lysatine were present in exceedingly minute quantities, if at all. It is possible that the small amount of nitrogen present was due to slight traces of peptones which tannin failed to remove.

Lysatine.

In Cheese Four and a Half Months Old.—To Solution B, obtained as described above, we added just enough barium nitrate to remove all sulphuric acid, filtered and concentrated the filtrate to small bulk. Silver nitrate was carefully added

until the presence of an excess was shown by the usual test, and then a few drops of dilute nitric acid were added. Alcohol was next added and a precipitate began to form, when the addition of alcohol was continued until its volume equaled the volume of the solution. Then a small amount of ether was added, when a crystalline precipitate was formed. This was allowed to stand twenty-four hours and then filtered, washed with ether, and dried over sulphuric acid, yielding a product weighing 2.1 grams. The filtrate was used for separating histidine. This product behaved like Siegfried's lysatine, and analysis shows its similarity to that body.

0.202 gram substance gave 0.0565 gram Ag.

0.214 gram substance gave 74.5 cc. N at 22° C. and 746 mm.

	Calculated for $C_6H_{13}N_5O_2HNO_3AgNO_3$.	Found.
Ag	27.51	27.97
N	17.90	17.89

A portion of the lysatine silver nitrate, obtained as described above, was treated with hydrochloric acid and evaporated nearly to dryness, this operation being repeated several times to remove the greater part of the nitric acid. Platinum chloride was then added and the solution evaporated nearly to dryness, when, on addition of alcohol, the platinum salt of lysatine separated. This was filtered, washed with alcohol, and dried over sulphuric acid *in vacuo*. Analysis gave the following results:

0.2414 gram substance gave 0.0835 gram Pt.

	Calculated for $C_6H_{13}N_5O_2H_2PtCl_6$.	Found.
Pt	34.28	34.58

Histidine.

In Cheese Four and a Half Months Old.—The filtrate obtained from the precipitate of lysine, as described above, was carefully evaporated on the water-bath to remove ether and alcohol, and then treated with barium hydroxide until 1 drop of the clear supernatant liquid, added to an ammoniacal solution of silver nitrate, gave no precipitate, thus showing the complete precipitation of histidine. This precipitate was fil-

tered, washed with water, and then suspended in water and treated with hydrogen sulphide to remove silver. After the silver sulphide was filtered, the filtrate was evaporated to dryness, this residue extracted with dilute silver nitrate containing a few drops of nitric acid, and the extract precipitated with ammonia, filtered, and washed with water. This precipitate was next suspended in water, decomposed by hydrochloric acid, the silver chloride filtered and washed, and the filtrate concentrated and allowed to stand several days, when crystals began to separate. After standing a few days longer the liquid was filled with crystals. The crystalline mass was washed with ether and dried over sulphuric acid, *in vacuo*, yielding 4.1 grams histidine.

0.374 gram substance gave 0.1156 gram Cl.

0.2918 gram substance gave 0.532 gram N.

	Calculated for $C_6H_9N_3O_2HCl$.	Found.
Cl	31.11	30.93
N	18.42	18.23

Arginine.

In Cheese Four and a Half Months Old.—The filtrate from the histidine precipitate was saturated with barium hydroxide, the precipitate filtered, washed with a solution of barium hydroxide, suspended in water, acidulated with sulphuric acid, and the silver removed by hydrogen sulphide. The entire filtrate contained only 0.085 gram nitrogen, equivalent to 0.255 gram arginine. The amount was too small to obtain a crystalline product, and we are led to conclude that arginine does not exist in appreciable quantities in cheese of this age. Winterstein and Thöny[1] have also reported a similar result in case of Emmenthaler cheese, the age of which, however, they do not state.

Lysine.

Solution A, obtained as described above, was freed from barium by sulphuric acid and from silver by hydrogen sulphide, and the filtrate from these precipitates concentrated to small volume. The solution was made to contain 5 per cent

[1] Ztschr. physiol. Chem., 36, 28 (1902).

of sulphuric acid and precipitated with phosphotungstic acid. The precipitate was filtered, washed with dilute sulphuric acid, suspended in water, decomposed by barium hydroxide, filtered, and the excess of barium removed by carbon dioxide, the solution then being concentrated to small volume.

In Cheese Fifteen Months Old.—To the solution thus concentrated, alcohol of 95 per cent strength was added in quantity equal to twice the bulk of the solution. Picric acid was then added. On standing twenty-four hours no precipitate appeared. The alcohol was then evaporated, the solution concentrated, and a saturated solution of picric acid added, when crystals began to appear, and increased considerably on standing over night. The crystals were filtered, washed with cold water, recrystallized four times from water, finally washed with ether and dried over sulphuric acid, yielding 9.2 grams (Fraction No. 1).

The filtrate from the first fraction of crystals was further concentrated by evaporation and more picric acid was added, producing a small additional yield of crystals. These were filtered, washed with ether and alcohol, and dried over sulphuric acid, yielding 0.8 gram (Fraction No. 2).

The last filtrate was further concentrated by evaporation, when a slimy precipitate separated. The whole mixture was then shaken with ether in sulphuric acid solution in order to remove all picric acid, after which it was repeatedly boiled with animal charcoal and filtered to remove all coloring-matter. The solution was then reprecipitated by phosphotungstic acid, the precipitate decomposed by barium hydroxide, filtered, and excess of barium removed by carbon dioxide , the resulting solution being concentrated to small bulk by evaporation. Alcohol was added equal in amount to twice the volume of the solution and picric acid carefully added. A crystalline precipitate began to form and increased on standing. After twenty-four hours the crystals were filtered, washed with alcohol, recrystallized three times from water, finally washed with ether and dried over sulphuric acid, yielding 14.1 grams (Fraction No. 3).

The last filtrate was further concentrated by evaporation

and yielded an additional crop of crystals, weighing 0.2 gram (Fraction No. 4).

The crystals contained in Fractions 3 and 4 behaved like lysine and showed, on analysis, a composition corresponding to this compound.

	Calculated for $C_6H_{14}N_2O_2C_6H_2(NO_2)_3OH$.	Found.
N	18.66	19.17
C	38.40	38.18
H	4.53	4.21

On converting this salt to a chloride and estimating the chlorine, the following results were obtained:

0.277 gram substance gave 0.3616 gram AgCl.

	Calculated for $C_6H_{14}N_2O_2HCl$.	Found.
Cl	32.39	32.24

In Cheese Four and a Half Months Old.—We obtained 5.4 grams of lysine. A portion recrystallized several times from water gave 18.81 per cent nitrogen, the calculated amount being 18.66 per cent nitrogen.

Tetramethylenediamine (Putrescine).

In Cheese Fifteen Months Old.—Fraction No. 1 of crystals, obtained as described above, resembled tetramethylenediamine in its solubilities, and an analysis showed its identity in composition with this compound.

	Calculated for $C_4H_{12}N_2C_6H_2(NO_2)_3OH$.	Found.
N	20.51	20.34
H	3.29	3.48
C	35.16	35.40

On converting this compound to a chloride, the following amount of chlorine was obtained:

0.206 gram substance gave 0.365 gram AgCl.

	Calculated for $C_4H_{12}N_2HCl$.	Found.
Cl	44.06	43.76

In Cheese Four and a Half Months Old.—We expected to find putrescine in this cheese as in the other, since arginine, of which it forms a reduction-product, was not found, but we were unable to obtain this compound.

Isolation of Ammonia from Ripening Cheese.

We ground with sand 500 grams of a normal cheddar cheese, ten months old, ripened at 13° C. We extracted this with water at 55° C., precipitated the water-extract with tannin, filtered and distilled the filtrate with steam into a dilute solution of hydrochloric acid. The distillate was evaporated after addition of platinum chloride and the ammonium salt isolated, yielding 8.1 grams of ammonium chlorplatinate. After drying over sulphuric acid the following analytical results were obtained:

	Calculated for $(NH_4)_2PtCl_6$.	Found.
Pt	44.21	44.22

Since we have found in the cheese fifteen months old the volatile base putrescine, it was thought possible that small amounts of this base might distil over when the estimation of ammonia is made by distillation with magnesium oxide, thus vitiating the results in the ordinary method of estimation by increasing the amount of nitrogen obtained as ammonia. In the case of the cheese used and under the conditions of experiment, no such contamination was observable.

Discussion of Results.

Summarizing the results secured by the work embodied in the preceding portion of this paper, we find (1) paranuclein as a common constituent of all cheeses examined by us; (2) in the younger cheese, which was four and a half months old, the three basic products, lysatine, histidine, and lysine; and (3) in the older cheese, which was fifteen months old, tetramethylenediamine (putrescine) and lysine.

In neither case were we able to separate arginine, but in the older cheese we found putrescine, one of the reduction-products[1] of arginine. We did not look for guanidine, but this compound might be expected to be present as the other cleavage-product of arginine, and Winterstein and Thöny have reported its probable presence in Emmenthaler cheese. While there is some reason to believe that lysatine is com-

[1] Ellinger: Ztschr. physiol. Chem., 30, 334 (1900).

posed of arginine and lysine, the point is not clearly settled, and in our discussion we have not assumed this to be the case.

It is known that lysine yields also pentamethylenediamine (cadaverine) on reduction, and Winterstein and Thöny have reported the presence of the latter compound in an Emmenthaler cheese. They do not give any facts in relation to the history of the cheese used in their work, and we are unable, therefore, to make any comparison with our cheese fifteen months old, in which we found one of the reduction-products of arginine, *viz.*, putrescine. Whether cadaverine might have been formed ultimately we cannot say.

There appears to be good evidence that there is regularly in the cheese-ripening process, in the case of hard cheeses like Emmenthaler and American cheddar, a conversion of primary into secondary amido compounds, and these chemical changes may explain, perhaps, the gradual development of flavor in normal cheese; in other words, we may find that the changing flavor of cheese as it ages is due, to some extent, to increasing quantities of secondary amido compounds.

In flavor, the older cheese used by us was rather pungent, but not unpleasantly so. It had a high ammonia content, which is a marked characteristic of cheese ripened at temperatures above 15° to 18° C., and which also is a usual accompaniment of a pungent flavor. In cheese ripened in cold storage, where the temperature is usually below 5° C., small amounts of ammonia are formed and the flavor is very mild. We must bear in mind, however, that the presence of mere traces of such compounds as putrescine, cadaverine, and ammonia will not suffice to account for marked abnormal sharpness or other unpleasant quality of flavor in cheese, but that they gradually accumulate and, finally, are present in quantities such that we might expect them to predominate and impart to the cheese mass the flavors peculiar to them.

In cheese, technically known as "gassy," characterized by formation of considerable quantities of different gases, hydrogen forms a part of the gas, so far as examinations that have been made show, and this gas can be regarded as an agent easily capable of favoring the early formation of the reduc-

tion-products that have been found, *viz.*, putrescine, cadaverine, and ammonia.

The subject of cheese flavors is one of complex difficulties, but it is safe to say that these flavors are due to the presence of specific compounds, and any work that shows in cheese the formation and presence of compounds capable of imparting flavors will contribute to the solution of a problem whose details are now little understood.

GENEVA, N. Y., Nov. 20, 1902.

ON THE EXISTENCE OF PERCHROMIC ACID.

BY HARRISON EASTMAN PATTEN.

It has been established by A. Bach[1] and confirmed by Baeyer and Villiger,[2] that hydrogen peroxide may contain more oxygen than is required by the formula H_2O_2. Bach maintains that chemical union exists between the excess of oxygen and the hydrogen peroxide to form H_2O_4. Berthelot[3] held to this same explanation. Baeyer and Villiger,[4] on the same basis of fact, claim that the excess of oxygen is merely "dissolved" in the hydrogen peroxide solution in water, giving a solution supersaturated with respect to oxygen.

I have repeated many times a simple qualitative experiment bearing on this discussion, and always successfully. Potassium dichromate is dissolved in water to saturation, cooled to —16° C. by ice and salt, and treated with a 2 per cent aqueous solution of hydrogen peroxide, also at —16°. Two actions are observed: (1) A white solid separates from the solution, doubtless a combination of potassium; (2) the solution turns blue. When a cold, saturated, aqueous solution of sodium acetate is added to this solution, the lake color of chromous acetate is at once taken on by the solution. On standing half an hour the green color of chromic acetate appears.

Solid chromous acetate was obtained by treating the blue aqueous solution first formed with cold ether, separating, and

[1] Ber. d. chem. Ges., 33, 1506 (1900).
[2] *Ibid.*, 33, 2488 (1900).
[3] Ann. chim. phys., [5], 21, 176.
[4] *Loc. cit.*

adding solid sodium acetate to the blue ethereal solution. In contact with the ethereal solution, solid chromous acetate is rapidly oxidized to chromic acetate. The electrical conductivity of a strong blue ethereal solution of chromous oxide —as I shall call it—was found to be less than 2×10^{-8} reciprocal ohms at about 0° C. This experiment was first carried out January 30, 1902.

It will hardly be maintained that the sodium acetate reduces the "perchromic acid," said to exist in this blue ethereal solution, to the chromous state. It appears unlikely, too, that chromous chromium would exist in a solution supersaturated with oxygen, as Baeyer and Villiger claim. The simplest explanation of the facts is that hydrogen peroxide reduces the chromic acid to the chromous state, and forms a higher oxide of hydrogen. Bach's position, that this higher oxide of hydrogen is combined with the chromous oxide, is tenable to the extent that all solutions are combinations of solute with solvent.

The desirability of analyzing the chromous acetate formed here, I fully appreciate. That it is chromous acetate there can be no doubt. I feel that this reaction should be made known now ; later, if no one else has worked upon it, I shall make the analysis, though the speed with which the acetate changes from chromous to chromic renders this difficult. In all probability the reaction between hydrogen peroxide and potassium permanganate takes the same course as that with potassium dichromate, as Berthelot[1] stated in the first place.

This formation of chromous acetate from the blue aqueous and ethereal solutions of chromous oxide and H_2O_x confirms the existence of an oxide of hydrogen higher than H_2O_2, and renders the existence of perchromic acid extremely doubtful, especially as all electrolytic attempts to prepare it have failed in this laboratory and elsewhere.

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MADISON, Oct. 27, 1902.

[1] *Loc. cit.*

REPORT.

The Luminosity of Mantles.

The great increase in the luminosity and the stability of the incandescent gas mantles and their ever-increasing use have directed the attention of many investigators to this subject, and efforts have been made to improve upon the results already obtained and to discover other methods and substances which would produce the same results.

A knowledge of the cause of the luminosity would be of fundamental importance in any investigations undertaken to devise new methods or improve old ones, and in the course of these investigations a number of observations have been made which have led to a very satisfactory explanation of the remarkable luminosity of these mantles. Although it has been known for some years that many refractory bodies emit light, when heated to a high temperature, no successful application was made of these observations, except in the use of the Drummond light, until the introduction of the Welsbach mantle about twelve or fifteen years ago. Berzelius had noticed, in the early part of the nineteenth century, the marked incandescence of certain oxides and supposed it to be due to the high temperature alone. Talbot,[1] in 1835, stated that paper soaked in calcium chloride and burned leaves a white network of ashes, which emits a brilliant light. A few years later Cruickshank patented a cage of fine platinum wires which could be suspended in the flame and be heated to incandescence. He attempted to increase the luminosity by coating the wires with a paste of oxides, but found it impossible to make the oxides adhere. In 1852 Bergmann noticed the incandescence of oxide of thorium, and in 1864 Bahr[2] and Bunsen published the results of an investigation in which it was shown that the oxides of the yttrium group of metals, when heated to incandescence, emit a light of great intensity. In a recent article Auer von Welsbach[3] describes his efforts to obtain a practical mantle and his persistence in the experiments, even after all his financial backing had been withdrawn, the factory closed, and the staff of assistants dismissed. Success finally crowned his efforts, and by the continued work of the skilful chemists employed by the company bearing his name the mantles have reached their present perfection. The explanations, which have been offered, of the cause of the

[1] Phil. Mag., 3, 114 (1835).
[2] Ann. Chem. (Liebig), 132, 227.
[3] Chem. News, 85, 254.

luminosity have been based either on a physical cause, ascribing it to the temperature alone, or on a physical-chemical one, in which case it is considered to be due to the catalytic action of one of the constituents or to an oscillatory oxidation. Drossbach ascribed the action to a peculiar power which the ceria possessed of converting heat rays into light rays, while Westphal called attention to the fact that we are dealing with a basic and an acidic oxide, and that the peculiar manifestation of energy was perhaps due to the slow combination of the two oxides.

Killing[1] has pointed out that the mixtures which have been used for mantles contain one substance which is capable of more than one degree of oxidation and that the ceria in the Welsbach mantle and the chromium oxide in the Sunlight mantle can, by successive oxidation and reduction, increase the flame temperature and the luminosity. If this is the only action involved we might expect to find an increased luminosity with an increase in the proportion of ceria, but Hintz has shown that the addition, above a certain amount, diminishes the luminosity, as the following figures show:

Thoria. Per cent.	Ceria. Per cent.	Candle power.
99.5	0.5	11.6
99.0	1.0	17.8
98.0	2.0	15.3
95.0	5.0	10.0
90.0	10.0	2.7

Wyrouboff, Armstrong,[2] and von Welsbach[3] likewise ascribe the effect to a successive oxidation and reduction.

Bunta[4] considers the effect to be due to catalytic action of the ceria. The thoria forms a porous oxide which is a poor conductor, while the ceria forms a dense oxide which is a good conductor and which has the power to condense the gases on its surface and produce the intensifying effect, when these gases combine, over a large surface area.

Among the investigators who have explained the results as due to the effects of temperature alone, Nernst and Le Chatelier have been especially prominent.

Nernst[5] compared the light from the mantle with that from a black body (electric light), and found that the mantle gave the most intense light in the yellow and violet portions of the

[1] Jour. f. Gasbeleuchtung, 1896.
[2] Proc. Roy. Soc., 70, 99.
[3] Chem. News, 85, 254.
[4] J. Soc. Chem. Ind., 1898, 229.
[5] Physik. Zischr., 1900, [26], 289.

spectrum and emitted fewer heat rays than other substances at the same temperature.

On account of this action the mantle is heated to a high temperature and emits light in that portion of the spectrum which produces the strongest visible effect. In order to show that the luminosity is not due to the gases with which it is in contact, Nernst heated one mantle by the gas flame and another by the electric current, keeping the two at the same temperature by regulating the resistance, and found no difference in the results, but Bunta denied the justice of entirely excluding catalytic action, in some part of the flame, from the possible causes, as he showed that the mantles could be heated to incandescence if introduced into the cold mixture of gas and air. Le Chatelier[1] says the mantles become as incandescent when heated in the hot products of combustion of the flame as when placed in the burning gases themselves. The proportion of energy radiated as visible rays is very high, and while the absolute amount of energy is less than that of a black body raised to the same temperature, yet the black body under the same conditions and with the same surface area actually reaches a much lower temperature and therefore gives less light. Bunta has found, however, that such widely different bodies as carbon, magnesia, ceria, etc., when heated out of contact with the air, showed very little difference in the amount of light radiated, and Swinton has found that while there was a difference in the ease with which they could be heated in a vacuum, by bombardment, yet the amount of light emitted in the different cases was about the same.

The point raised by Nernst and Le Chatelier has been tested by White, Traver, and Russell,[2] and by Féry,[3] who found that an increase in temperature alone will not suffice to explain the results obtained. White and Russell found that with any one mantle the luminosity did increase with the temperature as Le Chatelier claimed, but if his view is correct a slight change in the composition of the mantle should not cause any marked difference in the result. That there is a considerable difference, not only in the temperature of the mantle and the flame surrounding it, but even in the mantles of different composition, without causing a corresponding change in luminosity, is clear from the determinations made with a carefully calibrated and standardized thermo-couple, which indicated a temperature of 1523° on the inside of the mantle at a distance of 1 mm. from its surface, while the mantle itself only reached a tem-

[1] J. Soc. Chem. Ind., 1898, p. 1129.
[2] *Ibid.*, 21, 1012; Amer. Gaslight J., 74, 488.
[3] Ann. chim. phys., [7], 27, 433.

perature of 1373°. The following table will show in a marked degree the effect of composition on the luminosity :

	Mantle I. Pure ThO_2.	Mantle II. 99.5 per cent ThO_2 and 0.5 per cent Ce_2O_3.
Temperature	1510°	1404°
Illum. value	1.2 candles	15.7 candles

These facts are in direct opposition to the view of Nernst and Le Chatelier, for, with a temperature 100° lower in mantle II., the luminosity is thirteen times greater. White and Russell consider the ceria to be present as a solid solution in the thoria and to act as a very economical transformer of heat into light. A mantle made from a mechanical mixture of the oxides increased in luminosity, after some hours, more than one made from the mixed nitrates. If the mixture was gradually converted into a substance similar to the mantle and if at the same time the luminosity increased, the Le Chatelier theory, which was based on the observation that couples coated with the oxides from mantles attained a higher temperature and gave more light than when coated with any other substance under the same conditions, would appear to be in accord with the facts, but all the experiments made by the authors showed that in every case the one with the lower temperature gave the most light.

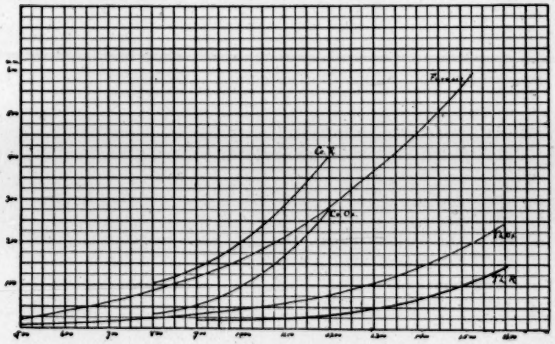
Féry has determined the total heat and light rays emitted by black bodies and white oxides, and by the application of the results obtained has been able to offer an explanation which is apparently in agreement with the known facts. To measure the heat radiations he selected a thermo-couple made of iron and constantan (an alloy of copper and nickel) with a silver plate at the junction. The couples were mounted in a tube at the point where the rays were brought to a focus by a lens of fluorspar. The best dimensions of the couple were carefully determined, as was the absorption value of the lens, and a special very sensitive form of galvanometer was used to indicate the small currents set up in the couple. The determinations were first made in terms of the amount of deviation of the mirror and later reduced to absolute values, using a standard whose value could be determined. The substance under investigation was molded in the form of a cup and attached to the axle of a motor, revolving about 200 times a minute, so as to become evenly heated by the flame of a blast-lamp.

At the moment when the heat radiation was determined the temperature of the material was recorded by a galvanometer attached to a couple which was in contact with the cup. One

very interesting fact brought out in these comparisons was the marked difference, in some cases, in the heat radiation when the substance was heated in the oxidizing and reducing flames. The following table will give some idea of the relative values at different temperatures, the figures representing the relative deviation of the mirror:

	900°.	1000°.	1100°.	1200°.	1300°.	1400°.	1500°.	1600°.	1700°
Chromium oxide	138	188	252	334	437	564	710	...	...
Carbon	145	192	250	320	410	520	...	...	...
Platinum	22	30	40	54	72	96	123	152	...
Lime { Oxid.	12	15	20	26	37	54	86	134	216
Lime { Red.	12	15	20	25	32	42	54	71	90
Magnesia	33	42	52	65	83	106	140	186	204
Lanthanum oxide	33	44	57	76	100	136	180	246	354
Thorium oxide { Oxid.	28	50	56	78	108	142	184	228	...
Thorium oxide { Red.	18	24	30	38	50	69	99	138	...
Cerium oxide { Oxid.	58	103	172	272	...	...	...	...	...
Cerium oxide { Red.	140	200	290	404	...	...	...	...	...
Auer mixture { Oxid.	50	76	116	166	240	354	490	...	...
Auer mixture { Red.	30	46	70	108	150	208	300	...	...
Electric furnace	122	166	219	287	362	450	561	700	863

The following curves will illustrate the great differences in the case of the oxides which are used in the mantles and show that the radiation in the case of the ceria, when heated in the reducing flame, is even greater than that of the electric furnace or black bodies at the same temperature:



That this result was not due to the oxides of carbon in the flame was shown by heating the material in a hydrogen flame, when the same results were obtained. With the material made from the mantle mixture the results are in their general nature similar to those with thoria, as the radiation is greater in the oxidizing than in the reducing flame.

The results obtained in the measurements of the luminous rays, using an incandescent lamp as a standard and a color screen which cut out all but two green lines, were calculated in terms of the candle power furnished in watts per centimeter according to the temperature. The screen used consisted of two green glasses superimposed, the first, a uranium glass, allowed three brilliant lines to pass, two green and a red, while the second absorbed the red. One of the green lines was quite bright and was the special one by which the eye makes photometric comparisons.

A comparison of these figures shows that while the black bodies, carbon and the electric furnace, radiate very little light, only about 0,005 candle per watt, the oxide of chromium, on the other hand, gives a triple effect, due, no doubt, to the phenomena of luminosity which it exhibits.

Platinum is not suited for use as a mantle on account of its low melting-point, as compared with the substances actually used, while the oxide of lanthanum, which radiates a very large amount of light, rapidly volatilizes in the air.

The Auer mixture furnishes more light in the oxidizing flame than the thoria in the reducing flame, and probably still more in the reducing flame, although the values could not be determined.

The relative intensity of luminosity of mantles made of thoria, ceria, and the Auer mixture is shown by the following values:

	Candle power.
Mantle of thoria	1
" " ceria	7
" " Auer mixture	70

This necessitates some explanation besides the mere condition of temperature produced by the flame. When a Bunsen flame is directed against the sides of a mantle of thoria, the interior blue cone, whose temperature is relatively low, only produces a dark spot on the mantle, but with the ceria a very different result is obtained. A very bright zone starts at the outside and passes towards the center, giving the general effect of particles of potassium nitrate thrown on heated charcoal. This action is repeated again and again, indicating a

Light Radiation at Different Temperatures.

		900°.	1000°.	1100°.	1200°.	1300°.	1400°.	1500°.	1600°.
Electric furnace		0.0000	0.00014	0.00037	0.0009	0.00214	0.0041	0.0073	0.0135
Corundum		0.00012	0.00026	0.00041	0.0018	0.0051	0.0127	....	....
Carbon		0.00009	0.00025	0.00071	0.00176	0.0035	0.0054	....	....
Chromium oxide		0.00012	0.00037	0.00121	0.00385	0.0086	0.0155	....	....
Platinum		0.0000	0.00064	0.00161	0.00447	0.0107	0.0207	0.0352	0.0521
Magnesia		0.0000	0.00025	0.00062	0.00165	0.00516	0.0127	0.0229	0.0346
Zirconium oxide		0.00024	0.00055	0.00158	0.0051	0.0162	0.0362	0.056	0.0895
Calcium oxide	oxidizing	0.0000	0.00093	0.00233	0.0031	0.00655	0.0149	0.0262	0.0384
	reducing	0.0000	0.0000	0.00081	0.00129	0.00225	0.00498	0.0197	0.0227
Lanthanum oxide	oxid.	0.00049	0.00304	0.0925	0.0216	0.0435	0.0709	0.0955	0.124
	red.	0.00049	0.00097	0.00264	0.00762	....	....	....	....
Cerium oxide	oxidizing	0.00028	0.00112	0.00206	0.00355	....	....	....	....
	reducing	0.00008	0.00016	....	....	....	....	....	....
Thorium "	oxidizing	0.00038	0.00081	0.00172	0.00495	0.0119	0.0238	0.0392	0.0556
	reducing	0.0000	0.00067	0.00186	0.00466	0.0148	0.0350	....	....
Auer mixture	oxidizing	0.00032	0.00085	0.00213	0.00618	0.0140	0.0273	0.0438	....
	reducing	0.00070	0.0021	0.0055	0.0129	0.0289	....	....	....

condensation of the gases of the flame and a combination with the excess of air. That the thoria and ceria have a different influence upon the combination of gases has been shown by Bunta, who found that while no difference was observed in the presence of thoria, the ceria, on the other hand, would, in the case of a mixture of hydrogen and oxygen, which in the presence of an inactive substance combines at 650°, cause the combination to take place at 350°. This phenomenon will also explain the high luminosity manifested by the mantle for, on account of the very rapid increase in luminosity with the rise in temperature, the mean ray measured at the mean temperature is greater than the ray which the body would furnish if the temperature were uniform and equal to the mean temperature indicated by the couple.

In studying the photographic prints of the heated mantles of thoria, ceria, and the Auer mixture the author found that the ceria appeared almost black and acted like the black bodies. Further experiments showed that the ceria, when photographed by the illumination of an electric arc, when hot, exhibited a power of radiation similar to black bodies, thus confirming results obtained by other methods.

The observations made during this investigation led to the following conclusions:

The ceria mantle gave no light on account of the reduction of temperature due to its very great power of radiation. It has been shown that the couple coated with the mantle material has a temperature of more than 200° below that of the uncoated couple, and it is also known that the luminosity decreases very rapidly with the decrease in temperature. In order to obtain a satisfactory illuminating effect from the ceria the threads of the material would have to have a very small dimension, as the loss of heat is not as great from small threads as from larger ones, an action the author considers due to the viscosity of the gas rather than to the conductivity of the material.

The thoria acts as a support for the ceria, which, owing to its preparation from the mixture of nitrates of cerium and thorium, is in a very fine, spongy form. On account of its porosity it permits the gases to come in contact with the ceria, which has a catalytic action. Owing to its transparency it permits the rays to pass, and finally its great solidity enables it to keep the ceria in its original position and form. Another property of the thoria which is of great importance here is its very weak power of radiating heat, thus enabling it to heat up the ceria, which radiates very rapidly, to a high tem-

perature, which is still further increased by the combustion taking place through the catalytic action of the ceria.

At the temperature of 1200° the radiation of the thoria is ten times less than that of the ceria, and this difference is probably even greater at the elevated temperature which the mantle acquires in its normal working.

In all the mixtures used for mantles the two substances, a radiating one and a supporting one, have been used.

J. E. G.

REVIEWS.

MONOGRAPHIEN ÜBER ANGEWANDTE ELEKTROCHEMIE, IV. BAND. EINRICHTUNGEN VON ELECTROLYTISCHEN LABORATORIEN, unter besonderer Berücksichtigung der Bedürfnisse für die Hüttenpraxis. Von H. NISSENSON, Director des Central-Laboratoriums der Aktiengesellschaft zu Stolberg und in Westfalen. Mit 32 in den Text gedruckten Abbildungen. Druck und Verlag von Wilhelm Knapp. Halle a. S. 1903. pp. 51.

This little monograph discusses briefly certain questions connected with electrolysis, the fundamental laws of applied electricity, and a number of matters essential to electrolytic work, such as sources of current, current regulators, measuring apparatus, etc. The larger part of the work, however, is devoted to the description of laboratories in which electrolytic work is done. These include Aachen, Breslau, Clausthal, Darmstadt, Freiberg, Giessen, Königsberg, Lüttich, Munich, University of Pennsylvania, etc. H. C. J.

BAND V. HERSTELLUNG VON METALLGEGENSTÄNDEN AUF ELEKTROLYTISCHEN WEGE UND DIE ELEKTROGRAVÜRE. Von DR. W. PFANHAUSER, Fabrikant von Maschinen, Apparaten und chemischen Präparaten für Elektroplattierung, Galvanoplastik, und Metallpolierung. Mit 101 in den Text gedruckten Abbildungen. Verlag und Druck von Wilhelm Knapp, Halle a. S. 1903. pp. 144.

As would be inferred from the title, the work is chiefly of technical importance. Certain of the processes described are, however, of general interest. The ground covered by the monograph can be readily seen by referring to some of the chief headings in the table of contents. The author discusses the physical properties of copper precipitated electrolytically, the preparation of metal powder, the preparation of metal foil, the preparation of wires, the preparation of tubes, electrolytic etching, electrogravure, etc. H. C. J.

QUALITATIVE ANALYSIS. A manual for the use of students in schools and colleges. By L. M. DENNIS, Professor of Analytical and Inorganic Chemistry, and THEODORE WHITTLESEY, Instructor in Analytical Chemistry, Cornell University. Ginn and Co.: Boston. 1902.

This is a new manual. The authors desired "to prepare

a work on qualitative analysis that shall be exact and compendious, avoiding, on the one hand, the diffuseness of the larger treatises, and on the other, the incompleteness of the smaller manuals." The very explicit directions for the separation of the elements are followed in each case by discussions of the methods used, their difficulties, and the reasons for preferring these methods, with references to the literature of the subject.

In brief, the book is short enough to use in the average college course, the methods are thoroughly up-to-date, while the discussions raise the book above the mechanical level and will interest the thoughtful student. The reviewer considers it one of the best manuals.

ELEKTRO-METALLURGIE. Die Gewinnung der Metalle unter Vermittlung des elektrischen Stromes. Von DR. W. BORCHERS, Professor der Metallurgie und Direktor des Laboratoriums für Metallhüttenwesen und Elektrometallurgie an der Königlichen Technischen Hochschule zu Aachen. Dritte vermehrte und völlig umgearbeitete Auflage, erste Abtheilung, mit 169 Text-Abbildungen. Leipzig. 1902. Verlag von S. Hirzel.

The new edition of this excellent book is much fuller than the second edition. The first part of the work which has appeared in the third edition deals with the metallurgy of magnesium, lithium, sodium, potassium, aluminium, the cerite metals, copper and nickel. This is less than half the number of metals which will be dealt with when the work is completed, judging from the contents of the second edition.

Any work on the subject of electrometallurgy which comes from Borchers will be accepted as "standard" in its field.

H. C. J.